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PREFATORY NOTE.

SEVERAL of the author's students have taken an active interest in the production of this monograph. Mr. C. J. Peddle, M.Sc., has supplied the diagrams; Mr. C. T. Pollard, M.Sc., and in a very large measure Mr. C. C. Bissett, B.Sc., B.Met., have assisted in compiling the data contained in the Appendix; whilst the task of sorting and arranging these data has been carried out by Mr. S. English, M.Sc. To all these gentlemen the author expresses his hearty thanks.

The author will be glad to have his attention called by investigators to any work bearing on the subject of this monograph.

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CHAPTER I.

INTRODUCTORY.

In its widest sense, the term *association* embraces the whole of the phenomena of chemistry and various sections of physics. The smallest chemical unit, the atom, is made up, according to modern views, of associations of electrons the number and arrangement of which give the character to the individual atom; and by the association of these atoms, molecules composed either of similar or unlike atoms may be built up.

The subject of this monograph is concerned with the behaviour of the molecule, the dependence of its degree of complexity on the nature of the constituent atoms, and on the forces which act on it from without.

The molecule of an elementary substance may be of the simplest possible character like that of helium, monatomic; or, on the other hand, it may be of great complexity, like that of sulphur, which in the state of vapour near the boiling point of the substance, possesses on the average about eight atoms * in the molecule. Under the action of certain forces, however, such as heat, pressure, electrical stress, and solvent action, it is possible to reduce the size of the molecule, so that sulphur, for example, eventually even becomes monatomic. A substance such as sulphur at comparatively low temperatures has molecules which are associations of small ones, S_6, S_2, and S_1, as will be shown later; it is, in short, an associated substance. The molecules of certain compound substances are likewise associated, such as those of aluminium chloride or arsenious oxide, and it is usually possible to split or *dissociate* such molecules into two or more like parts. Such a dissociation does not occur completely at some one point, but takes place gradu-

* More correctly the vapour is a mixture of S_8 and S_6 molecules (see chap. II.).

ally, so that over a considerable range a mixture of different kinds of molecules is obtained. This is true of all states of matter and all kinds of dissociation.

There is a second form of dissociation of a compound molecule which can take place whether the molecule is originally an association of smaller, like, or of unlike molecules. Nitrogen peroxide, for example, gradually dissociates with rise of temperature so that from one molecule N_2O_4, two like molecules NO_2 are obtained. This process is complete at about 150°. Above 150°, a further dissociation sets in, when nitric oxide and oxygen, two unlike molecules, are produced, nitrogen peroxide being completely broken down into these products at 620° (under atmospheric pressure).[1] The first type of dissociation may be called homogeneous, and it is with this type that the monograph is almost wholly concerned; the second, on the other hand, is heterogeneous dissociation. The relation of the two types, so far as is known, is the subject of one of the chapters of the book; but it may be pointed out here that the action of temperature and pressure in the two cases is similar.

Instances of molecular association in gas molecules were discovered quite early in the development of the atomic and molecular theories, as the result of vapour density determinations by Dumas and Mitscherlich, but were only clearly explained when Cannizzaro demonstrated how readily Avogadro's Hypothesis acted as a guide in the comparison of gas molecules. The general acceptance of the hypothesis naturally paved the way for the active investigation of the molecular state of gases and vapours, and towards this end, the invention of a simple form of apparatus by Viktor Meyer greatly assisted. From about 1880 onwards for some fifteen or sixteen years, Meyer and his co-workers, as well as Biltz, Nilson, and Pettersson, and others, who used either Meyer's or Dumas' apparatus, amassed a large amount of data relating to the vapour densities of metals, non-metals, oxides, and salts, data which were particularly valuable from the point of view of valency, the Periodic Table and particularly the variation of molecular weight with temperature. The form of the apparatus was gradually improved until temperatures up to about 1700°-1800° could both be attained and utilized. No considerable further advance was made, however, until Nernst introduced the method of electrical heating, and apparatus

of iridium, by means of which investigations were made possible up to temperatures exceeding 2000°. The extent to which our knowledge of the subject has followed the invention of new apparatus is again illustrated by the invention of the glass spiral manometer and its improved forms, which now enable densities of vapours at various temperatures and pressures to be measured with greatly increased accuracy.

While Meyer and others were actively engaged in the study of molecular weight at high temperatures, the investigations by Raoult[2] on the freezing points and vapour pressures of solutions provided a means of determining molecular weights at comparatively low temperatures; and the extension of the gas laws to solutions by van't Hoff provided a theoretical basis for Raoult's generalizations and set a seal on the great utility of freezing point and vapour pressure measurements. Two series of abnormal substances soon came to light. Thus, Raoult found that his generalizations could not be strictly applied to aqueous solutions of electrolytes, for the depression of the freezing point was always abnormally great—for binary electrolytes in dilute solution, about twice the value found with non-electrolytes. On the other hand, a number of organic substances containing the hydroxyl group, when dissolved in solvents of the hydrocarbon type, depressed the freezing point less than was expected. According to the rules set out, therefore, it appeared as if a dissociation occurred in the first type, whilst in the second association took place, the molecular weight being greater than that corresponding to the simplest formula. To the second class, numerous examples of associated organic substances, alcohols, acids, and oximes were soon added as the result of the work of Paterno, Beckmann, Auwers, Fabyini, and Ampola and Manuelli. Recently, the behaviour of electrolytes has been studied much more completely and it has been shown that electrolytes are not only apparently dissociated in aqueous solutions, but also in certain other solvents, and that there is a gradual transition from dissociation to very marked association, according to the nature of the solvent. The molecular state in solution of elementary substances has likewise been studied by Raoult's processes, and it was in this country, quite early in the study of solutions, that the laws of Raoult were found to be equally valid for solutions of metals in metallic solvents; and

that, in consequence, the gas laws and Avogadro's Hypothesis could be applied to all types of solutions.

Methods for the investigation of pure liquids were only devised some years after it was possible to investigate solutions, although the properties of liquids had already been the subject of many investigations. To the question whether the size of molecules in liquids was the same as in the gaseous state, van der Waals, in 1876, replied that the continuous passage of a vapour into a liquid during which the relation between pressure and volume underwent no sharp change might be taken as indicating no alteration of molecular size. The first method of investigating molecular size was developed by Ramsay and Shields from previous deductions of Eötvös, and it was hoped that the method might be of very general application. Experience has shown that it breaks down outside a certain range of molecular weight. At the present time it must be admitted that although it is quite easy to detect association, the quantitative determination is another matter and there is often a big percentage difference between the results obtained by the many different processes of measurement that have been devised. There is great need of some guiding and reconciling principle like Avogadro's Hypothesis. With regard to the solid state, still less is known of molecular sizes, so little that no special section is called for in this monograph. The methods which have been proposed up to the present are extensions of those which yield results for liquids, and will be mentioned in the sections dealing with liquids.

The study of molecular complexity has had great influence on the progress of chemical theory. Reference has already been made to the density measurements of Dumas, made on mercury, iodine, sulphur, and phosphorus, and of Mitscherlich, on arsenic. Berzelius had previously, on the basis of Gay Lussac's Law of Volumes, believed that the relative densities of elementary gases were proportional to their atomic weights. Dumas and Mitscherlich showed that the atomic weights of mercury, sulphur, phosphorus, and arsenic so deduced were far different from the Berzelius' values found by chemical analysis; and Berzelius' atomic weight system falling into discredit, rival systems sprang up, none of which found general acceptance. Cannizzaro, introducing Avogadro's Hypothesis, explained the apparently con-

tradictory results with the elements named by giving a clear definition of the term molecule and of the relation of the atomic to the molecular weight. Different molecules, he demonstrated, had different degrees of complexity.

In the realm of solutions, too, the widely applied electrolytic dissociation hypothesis of Arrhenius attempted to explain the abnormal molecular weights of electrolytes in aqueous solution, whilst the phenomenon of osmosis has been explained by some chemists and physicists on the ground of association processes, both of like and unlike molecules.[3]

The newer theories of allotropy, too, are dependent on a study of molecular size. As a gas or vapour whose molecules can form aggregates contains, over a range of temperature, molecules of different sizes admixed, the proportions depending on the temperature and pressure, so also in liquids and solids such mixtures may exist. On this basis we have the theory of dynamic allotropy (chap. VIII.).

Finally we have chemical combination related in some way possibly to molecular association. This relationship forms the subject of the concluding chapter.

CHAPTER II.

MOLECULAR ASSOCIATION IN GASES.

In order to determine the molecular complexity of a gas, the molecular weight is found by means of a density measurement, and then compared with the simplest molecular weight obtained by chemical analysis; that is, compared with the sum of the atomic weights of the elements present. The method requires a knowledge of atomic weights, therefore, and for the elements which do not enter into chemical combination, recourse is had to a determination of the ratio, γ, of the specific heats of the gas or vapour, since for a monatomic gas $\gamma = 1{\cdot}67$, for a diatomic gas $1{\cdot}4$ to $1{\cdot}3$, and decreases in value as the molecule becomes more complex. The determination of γ, indeed, serves to indicate in a few cases (monatomic vapours, for which alone it is trustworthy) the complexity independently of the density.

The density may be determined with accuracy by Regnault's method, approximately by Bunsen's. Whytlaw-Gray and Ramsay,[4] for example, determined the density of niton by the former method; Debierne,[5] for the same substance, used the latter. At high temperatures (2000°) Bunsen's method has received considerable application by Emich.[6]

More frequently employed in the study of molecular complexity, however, are the methods of Dumas,[7] of Hofmann,[8] and of V. Meyer,[8a] particularly the first and last named, as both of them can be applied over a wide range of temperature. Of these two methods, that of Dumas can claim greater accuracy whilst the method of Meyer is more convenient.

The Dumas method, pretty much in its original form, has been made to yield results of fair precision by Biltz,[9] but its most important development lies in the introduction of a device by which the pressure of the vapour within the bulb can be registered. The device consists of a spiral of glass or of quartz, or of a quartz membrane, or yet again, as in the original

suggestion of Ladenburg and Lehmann, of a flattened glass or quartz tube, the essential condition of any of the forms being its sensitiveness to pressure. The method[10] can be illustrated by reference to the diagram of the apparatus (Fig. 1) employed by Preuner and Schupp, and to the following description.

The bulb A, in which the substance was vaporized, was made of quartz, and had an extension consisting of a flattened quartz tube B in the form of a spiral, which ended in a quartz thread carrying the mirror. From the box or chamber C containing this mirror, connexion was made to a pump by which the external pressure could be altered and a mercury gauge by which the pressure was measured. Into the quartz bulb, the volume of which with the extension was known, a known weight of the material was introduced, and, after the air had been exhausted, the bulb was sealed at *a*, and with the spiral, heated in an electrical tube furnace to the temperature required, the actual temperature being recorded by a thermo-couple inserted in the tubulure at *b*. When the pressure within the bulb A, and therefore, also the spiral, rises, the spiral tends to unwind and in so doing the mirror is deflected by an amount which can be read from a scale by a microscope. On the other hand, when an external pressure acts on the spiral, the compression of the latter reverses the direction of the mirror deflection. Hence, in the actual determination, after the mirror had been deflected by the pressure of the vaporized substance, it was brought back to the zero point by the gradual application of an external pressure, this pressure, measured on the gauge, being equal to the vapour pressure of the substance. By this process, therefore, all the required factors, the weight of substance, its

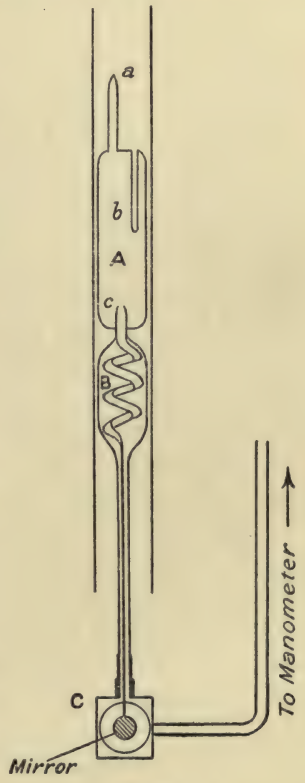

FIG. 1.

volume, temperature and pressure, were obtained with considerable accuracy.*

Although by the preceding method density determinations can be carried out at temperatures up to 1200°, when quartz is employed, and in the simple Dumas' form at still higher temperatures with a porcelain bulb, Meyer's method undoubtedly has the advantage in work at high temperatures. The older investigators obtained constant temperatures by using the vapour from boiling liquids such as aniline (184°), diphenylamine (310°), sulphur (445°), phosphorus pentasulphide (518°), and stannous chloride (606°), and, for still higher temperatures, specially constructed gas furnaces. But electrical heating, obviously more capable of regulation than gas, has been used in the experiments of Nernst[11] and of von Wartenberg,[12] in which temperatures exceeding 2000° were attained. For the measurement of the temperature, Meyer[13] and his co-workers adopted the device of utilizing the vaporization bulb both for its original purpose and as an air thermometer. The introduction of the thermo-couple and of the optical pyrometer has afforded more convenient methods of temperature measurement, although Meyer's device which consisted in expelling the residual filling gas by hydrogen chloride or carbon dioxide into a tube over potash, and from the volume of the gas so expelled (the original volume of the bulb and the coefficients of expansion of the gas and of the material of the bulb being known) calculating the temperature attained, was capable of considerable accuracy.

Modern methods may be illustrated by reference to the apparatus of von Wartenberg (Fig. 2). Since porcelain softens at 1700° so much as to require protection, and platinum melts at 1755°, the vaporization bulb was made of iridium, its size being reduced to 3-4 c.c. capacity. The temperature required was obtained by electrically heating an iridium cylinder enclosed in a mass of magnesia, current being supplied by water-cooled copper leads. The stem of the vaporization apparatus had five connexions, A to the nitrogen or argon supply which was to fill the tube after air had been removed by a mercury pump connected through B ; a tube C containing an arrangement, worked electro-magnetically, by which the stem could be closed at

* For a discussion of the errors involved the original papers of Ladenburg and Lehmann, Johnson, Preuner, Starck and Bodenstein, and Gibson should be consulted.

will; a manometer DE and the storage tube F containing weighed amounts of the substance in tiny capsules of ignited magnesia which could be pushed into the vaporization apparatus by an iron rod actuated from without by a solenoid. As the bulb of the apparatus was small, the amount of substance had

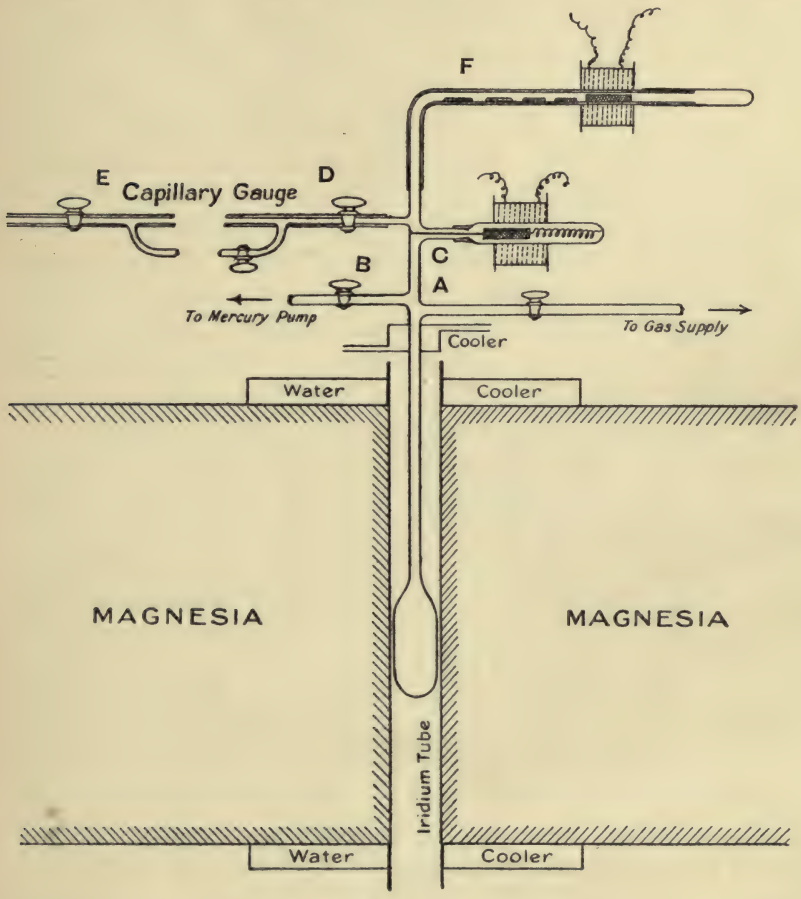

FIG. 2.

likewise to be reduced to a very small quantity, and the small expansion on vaporization was measured by the displacement in the calibrated capillary tube of the manometer of a drop of mercury moistened with sulphuric acid.

At high temperatures, metals become permeable to gases, and a glaze must be used as a protection. In von Wartenberg's

experiments, the bulb was coated within and without by a glaze of fused magnesia and magnesium chloride.

For the measurement of the temperature one of two methods was followed; either, an optical pyrometer was directed towards the bottom of the heated bulb, or, a rod of ceria and thoria was electrically heated until it glowed with a brightness equal to the bulb and the temperature of the rod measured optically.

The Molecular State of Gases and Vapours.

It will be convenient in giving an account of our present knowledge of the subject to quote first the results of measurements made on (*a*) elementary substances (*b*) compounds, and afterwards to deal more fully with the factors, namely, the temperature and the pressure influencing the molecular state.

Considering the elements as arranged in the groups of the Periodic Table, group O contains elements of the simplest molecular constitution. For the evidence of this we have to rely on determinations of the ratio of the specific heats from the velocity of sound. For helium, this ratio is 1·67,[14] for argon 1·659,[15] whilst the value for neon, xenon, and krypton is in each case approximately 1·66.[16] As the ratio should be 1·67 for a monatomic and very approximately 1·4 for a diatomic gas, the suggestion has been made that argon contains a very small percentage of diatomic molecules. At present there is no other evidence to support this suggestion.

Of the elements in Group I, only four, hydrogen, sodium, potassium, and silver have received any study as gases. According to Longmuir, hydrogen is appreciably dissociated when the temperature exceeds 2100° (abs.).[17] For trustworthy data on the alkali metals recourse must be had once again to the velocity of sound method, as all the density determinations appear to be open to criticism because of the corroding action of the metallic vapours.[18] Recently, Wenz [19] has carried out a determination of the value of γ for potassium vapour at a temperature of 850°, using a steel tube silvered within. The value obtained, 1·77, although high, is sufficient evidence of the monatomicity of potassium vapour, and there is little doubt that the other alkali metals are similarly constituted in the state of vapour. In regard to silver, von Wartenberg's vapour density determinations

at about 2000° [20] likewise indicate the monatomic state of the molecule, although the results are not sufficiently accurate to decide whether molecules of a higher order also exist.

From Group II onwards, our knowledge of the molecular complexity of the elements has been gained by vapour density measurements. It may be summarized in the following table:—

MOLECULAR WEIGHTS BASED ON VAPOUR DENSITIES.

Element.	Periodic Group.	At. Weight.	Temperature.	Molecular Weight.
Silver [20]	I	107·88	2000°	
Zinc [21]	II	65·37	1400°	68·0-69·6
,, [22]			1200°-2070°	66-76·7
Cadmium [23]	,,	112·4	1700°	126 and 127·2
,,			?	111·9
Mercury [24]	,,	200·6	?	199·6
,,			1952°	201-205
Thallium [25]	III	204	1320°-1690°	210-206
Lead [22]	IV	207·1	1600°	223
,,			1870°	210-239
Phosphorus [26]	V	31·04	800°-1700°	111·3-92·1
Arsenic [27]	,,	74·96	1700°	153·2-160·1
Antimony [22]	,,	120·2	2070°	122-139
Bismuth [22] and [26]	,,	208·0	1640°	292
,,			2070°	214-244
Sulphur [28]	VI	32·07	468°-606°	226-137
,,			1690°-2023°	59-54
Selenium [29]	,,	79·2	1750°-1800°	178
,,			2070°	114-121
Tellurium [29]	,,	127·5	1750°-1800°	264
,,			2070°-2100°	152-179
Chlorine [30]	VII	35·46	up to 1450°	normal
,,			$>1450°$	$<70·92$
,,			0°-300°	$>70·92$
Bromine [31]	,,	79·92	15°-750°	159·84
,,			800°-1050°	159·74-150·52
Iodine [32]	,,	126·92	650°-1400°	254°-144°

The table is constructed from values determined at or near the atmospheric pressure. Determinations at various pressures and temperatures have also been made on phosphorus, arsenic, sulphur, and selenium and will be referred to in a later section; but it may be said here that all these elements have complex molecules which decrease in size with rise of temperature and diminution of pressure, until, in the case of sulphur and selenium, monatomic molecules are produced.

The results may be generalized in two ways. In the first place they may be regarded as illustrating once again the difference between the characteristics of metals and non-metals. It is true that the inert gases of the atmosphere resemble the metals in having molecules of the simplest character, namely mon-

atomic, even at temperatures not far removed from their boiling points, but the other non-metallic elements are polyatomic, often diatomic, frequently, however, of a still higher order, so that at low temperatures the sulphur molecule contains eight atoms. There are but two substances with the properties of metals, antimony and bismuth, which have complex molecules, but the transition from the non-metallic to the metallic is nevertheless illustrated in the lower complexity of the bismuth molecule.

The results may also be reviewed from the standpoint of the Periodic Table. In the horizontal rows, elements to the left of Group V have so far as tests have been made monatomic molecules, elements in Groups V to VII polyatomic molecules, the maximum molecular complexity occurring in Group VI (sulphur and selenium). The ease with which a molecule can be split up depends also on the atomic weight of the element, as is illustrated by comparing arsenic, antimony, and bismuth, or, better still, by the halogen elements. Little is known of the molecular weight of fluorine, Moissan's [29a] determination of the density giving a value less than that corresponding to F_2. Chlorine, however, between 0° and 300° has an abnormally high vapour density, and the suggestion has been made that molecules Cl_4 [30a] are present to the extent of 3·33 per cent at 0° and 0·02 per cent at 300°. From this point up to 1450° the diatomic molecule is stable.[30] Bromine begins to split up into monatomic molecules at 750°-800° and iodine at a still lower temperature. Although molecular complexity tends to decrease in these cases with increase in mass, nitrogen and oxygen, first members of series of elements with complex molecules, are themselves only diatomic.

Compounds.

(*a*) *Metallic.*—

Substance.	Simplest Molecular Weight.	Observed Molecular Weight.	Temperature.
Silver chloride [13]	143·3	165	1735°
,, ,,		239	? (lower than 1735)
Cuprous chloride [33]	CuCl = 99·06	200	1560°
,, ,,		186	1700°
Glucinum chloride [34]	80·06	88·6-80·7	589°-812°
Aluminium chloride [35]	133·48	286·1-254·0	209°-440°
,, ,,		215·3-123·1	440°-1400°
Aluminium bromide [36]	266·9	540·2	440°
Aluminium iodide [36]	407·9	783·8	440°
Ferric chloride [33]	162·2	321·9-318·2	447°-619°
Ferrous chloride [37]	126·8	192·7-184·3	(yellow heat)
Stannous chloride [38]	189·9	253·2-204·6	639°-1113°
Mercurous chloride [39]	471	445	434·8°

In addition to the substances tabulated, quite a number of other metallic chlorides have been investigated, NaCl, KCl,[11] KI,[39a] $ZnCl_2$, $ZnBr_2$, $CdBr_2$,[33] $HgCl_2$, $GaCl_3$, $GaCl_2$, $InCl_3$, $InCl_2$, InCl,[51] $TlCl_2$, $PbCl_2$,[52] $ThCl_4$,[53] $CrCl_3$, $CrCl_2$,[51] but with the possible exception of $InCl_2$ and $GaCl_3$ there is no evidence of association. All the determinations save those of Nernst on sodium and potassium chlorides are not recent and might well be re-investigated by more accurate methods.

(*b*) *Non-metallic Compounds.*—

Substance.	Simplest Molecular Weight.	Observed Molecular Weight.	Temperature.
Water	18	(see p. 89)	
Hydrogen fluoride [40]	20	51·6-20·7	26·4-88·1
Hydrogen boride [41]	?	B_4H_{10}	
Hydrogen boride [41]	?	B_6H_{12}	
Acetic acid [42]	60·0	100·6-70·8	120°-180°
Metaphosphoric acid [43]	80·0	154 and 156	(? 1000°)
Nitrogen peroxide [44]	46·0	76·6-40·7	26·7°-154°
Phosphorous oxide [45]	110·1	224-225	132°-184°
Phosphoric oxide [43]	142·1	370-307	(? 1000°)
Arsenious oxide [46]	197·9	396-199	518°-1800°
Antimony oxide [33]	288·4	566-577	1500°
Nitrogen trioxide [47]	76·02	76·2-119·6	*ca.*20°

The metallic compounds which are known to be associated in the state of vapour cannot very well be classified. They are all halogen compounds, it is true, but the obvious reason is that they alone, among the salts, can be volatilized without decomposition. It might be thought likely that the alkali haloids would be among the associated vapours, since, as will be seen later, they are associated in solution and in the fused state; but the existence of associated molecules in the vapour depends largely on the temperature coefficient of association. Liquid water has complex molecules which are rapidly broken up by rise of temperature, so that in the vapour, only a small proportion of double molecules are present, whilst the effect of temperature variation on acetic acid is much less and the vapour is far richer in double molecules. Despite the highly complex state of the fused alkali salts, therefore, it is not surprising that at the temperatures at which they may be volatilized, no appreciable association occurs.

Of the non-metallic associated vapours, most of them contain oxygen. Most of them, too, contain as the other element,

or one of the elements, a member of Group V. The analogous oxides, nitrogen trioxide, phosphorous, arsenious and antimonious oxides are all associated. The effect of temperature alteration on nitrogen trioxide has not yet been worked out. Phosphorous oxide undergoes heterogeneous dissociation [45] when heated, so that the only formula which will fit the substance is P_4O_6. Mercurous chloride, of the metallic compounds, likewise yields $Hg + HgCl_2$, when heated. Although from Baker's work the likeliest formula is Hg_2Cl_2, later work makes this doubtful.[39] Cuprous chloride has not yet been broken down into CuCl molecules, nor have phosphoric oxide and metaphosphoric acid been split into smaller like molecules, so that their formulæ are Cu_2Cl_2, P_4O_{10} and $H_2P_2O_6$ respectively.

The Influence of Temperature on Molecular Complexity.

From the very many examples already provided, the effect of high temperatures in simplifying molecular aggregations will be apparent. Just above its boiling point, sulphur molecules are so complex as to be represented on the average by the formula $S_7 - S_8$; but at 1000°, simplification to a molecule S_2 has occurred, whilst at 1000° higher still, the cleavage of diatomic into monatomic molecules is well on the way. This gradual dissociation of a complex molecule is well illustrated by Biltz's measurements on arsenious oxide at atmospheric pressure. In the following table, the values of the vapour density (d) compared with air, are given. From them the molecular weight, if desired, can be obtained by multiplying by the factor 28·9.

Density of Arsenious Oxide.

$t°$.	d.	$t°$.	d.
518°	13·71-14·14	1450°	9·41
769°	13·62	1584°	8·80-8·83
851°	13·15	1732°	7·32
1059°	12·72-12·83	1800°	6·93
1256°	12·36		

Meyer believed that along the lines of high temperature measurement lay the hope of resolving the atoms of elements still further, and at the time of his death he had constructed a volatilization tube mainly of magnesia (88 per cent) for use at a temperature of 2000°.[48] But even the conversion of diatomic into monatomic molecules is in a number of cases far from complete at this temperature, and no further division by heat has been accomplished in the case of a monatomic vapour, such as

mercury; the molecular weight of this substance at 1952° being, according to Nernst, still 201-205, the same value as at 360°.

The degree of dissociation can readily be calculated from the densities observed. Suppose, for example, that N molecules of the original complex form have been heated up to a temperature $t°$, resulting in the dissociation of a certain fraction a (which fraction is the degree of dissociation), and that n simpler molecules result from the cleavage of each complex one. The number of molecules remaining undissociated will be $N(1 - a)$ and the number of simple molecules Nan. The total number of molecules, complex and simple, therefore, becomes

$$N(1 - a) + Nan = N[1 + a(n - 1)].$$

With the increase in the number of molecules, the density diminishes in proportion. Hence, if d_o and d_t are the densities of the undissociated and partially dissociated vapours, then

$$\frac{d_t}{d_o} = \frac{N}{N[1 + a(n - 1)]} = \frac{1}{1 + a(n - 1)} \quad . \quad . \quad . \quad (1)$$

$$\text{and } a = \frac{d_o - d_t}{d_t(n - 1)} \quad . \quad . \quad . \quad (2)$$

Since at every temperature the extent of dissociation has a definite value, the vapour of any dissociating substance consists of a mixture of different molecular forms. A reversible or equilibrium reaction thus exists, as in

$$I_2 \rightleftarrows I + I$$
$$N_2O_4 \rightleftarrows NO_2 + NO_2$$
$$(H_2O)_2 \rightleftarrows H_2O + H_2O$$

and so on, and the law of mass action requires that the quantitative relationship

$$Kp = p_1p_2 = p_1^2, \text{ shall hold,}$$

where p measures the partial pressure and therefore the concentration of the still undissociated molecules, and p_1 and p_2 (which in all the above cases are equal), the corresponding partial pressures of the single molecules.

The manner in which a given complex molecule breaks down can therefore be tested by the validity of the equation expressing the equilibrium between the components of the mixture; for the value of K, the equilibrium constant, must remain unchanged at constant temperature. Thus, Preuner and Schupp[10] concluded that the dissociation of the sulphur molecule proceeded in the stages

$$(1)\ 3S_8 \rightleftarrows 4S_6,$$
$$\text{and } (2)\ S_6 \rightleftarrows 3S_2,$$

because the equilibrium equations $K_1 = \frac{p_1^4}{P_1^3}$ for the first and $K_2 = \frac{p_2^3}{P_2}$ for the second were found to be true; that is to say, the values of K_1 and K_2 were found to be constant. A third stage at high temperatures or low pressures also occurs, namely, $S_2 \rightleftarrows 2S$; but the expression $K_3 = \frac{p_3^4}{P_3}$, corresponding to a dissociation $S_8 \rightleftarrows 4S_2$, was not found to hold, and hence this mode of dissociation was ruled out as unlikely. Rejected also as improbable were the degrees of complexity S_7 and S_5, whilst it was also impossible to reconcile the partial pressure measurements with the existence of S_3, a form analogous to O_3 suggested by Erdmann [49].

In a very similar manner, Preuner and Brockmöller [10] came to the conclusion that the stages in the decomposition of selenium and arsenic were

$$As_4 \rightarrow As_2 \rightarrow As_1$$
$$Se_6 \rightarrow Se_2 \rightarrow Se_1$$

and Stock, Gibson, and Stamm similarly decided that between 500° and 1200° and at pressures ranging from 100 mm. to 1000 mm. the only change in the phosphorus molecule was represented by the transformation

$$P_4 \rightleftarrows 2P_2.$$

A study of the value of the equilibrium constant may furnish information on the energy changes accompanying a transformation from one kind of molecule to another. For the alteration in the point of equilibrium by a change of temperature is reflected in the value of the equilibrium constant, this alteration being expressed by the well-known equation of van't Hoff,

$$\frac{d \log_e K}{dT} = -\frac{Q}{RT^2},$$

T being the temperature measured on the absolute scale, R the gas constant and Q the amount of heat absorbed by a gram molecular quantity of substance during transformation. From the gas densities, the value of K can be obtained simply. For if the reaction be of the type

$A_2 \rightleftarrows 2A$, then, as before,

$$Kp = p_1^2.$$

The total pressure P of the gas mixture is the sum of the partial pressures $p + p_1$, and these in turn are proportional to the number of molecules of each form present. If, therefore, the degree of dissociation be a, the total number of molecules will increase in the proportion of $N/N[1 + a(n - 1)]$ (Equation 1), or $1 : 1 + a$ since $n = 2$ in the case selected.

Hence,

$$p = P\frac{1 - a}{1 + a} = P\left(\frac{2d_t}{d} - 1\right) \text{ from Equation 2,}$$

$$\text{and } p_1 = P\frac{2a}{1 + a} = 2P\left(1 - \frac{d}{d_o}\right).$$

Hence, also,

$$K = \frac{p_1^2}{p} = \frac{4(d_o - d)^2 P}{(2d - d_o)d_o} \quad . \quad . \quad . \quad (3)^{50}$$

The value of Q, the latent heat of transformation, may now be calculated from the integrated form of the expression

$$\frac{d \log_e K}{dT} = -\frac{Q}{RT^2},$$

neglecting the small variation of Q with the temperature, namely,

$$\log K = \frac{Q}{RT} + \text{constant} \quad . \quad . \quad . \quad (4).$$

In this way the following values have been obtained:—

Transformation.	Q.
$N_2O_4 \rightleftarrows 2NO$	− 12,700 calorics
$(H_2O)_2 \rightleftarrows 2H_2O$	− 9,640 „
$Br_2 \rightleftarrows 2Br$	− 55,300 „
$I_2 \rightleftarrows 2I$	− 28,500 „
$3S_8 \rightleftarrows 4S_6$	− 29,000 „
$S_6 \rightleftarrows 3S_2$	− 64,000 „
$P_4 \rightleftarrows 2P_2$	− 49,300 „

The Influence of Pressure.

Although there are certain cases of dissociation (heterogeneous), such as $2HI \rightleftarrows H_2 + I_2$ on which pressure alteration has no effect because the number of molecules taking part in the direct and reverse reaction is the same, this never applies to homogeneous dissociation, which is under discussion in this chapter, as will be evident from the many examples quoted in

the preceding section. Recently most of the investigators of the dissociation of gas molecules have studied the simultaneous

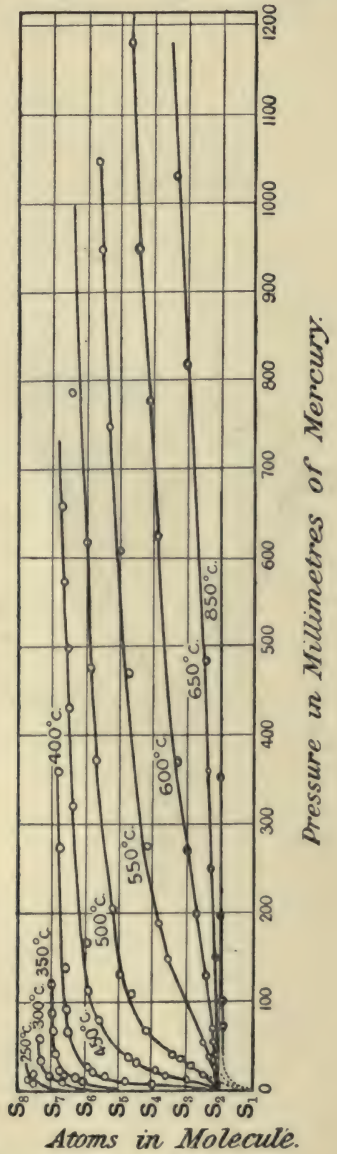

FIG. 3.

effect of both temperature and pressure. Fig. 3 represents in graphic form Preuner and Schupp's results of the study of sulphur vapour under these conditions, and it will be seen that

even at 850° when the pressure is below 100 mm. the final stage in the dissociation is in progress.

Instead of utilizing these data to deduce the constants concerned, the influence of pressure on the dissociation of phosphorus vapour (Stock, Gibson, and Stamm) will be chosen for illustration. The value of the equilibrium constant is given by equation (3) and when known, it is possible to calculate the density of the substance at any temperature and pressure, since from

$$K = \frac{4\,(d_o - d_t)^2\,P}{(2d_t - d_o)\,d_o}, \text{ we obtain}$$

$$d_t = d_o - \frac{Kd_o}{4P}\left[\sqrt{1 + \frac{4P}{K}} - 1\right]^* \quad . \quad . \quad . \quad (4)^{50}$$

In the following table are the values of K, of a, the degree of dissociation of the P_4 molecule, and of d_t observed and d_t calculated, using in the calculation, the mean value of K for the given temperature.

$t°$.	a.	P.	K.	d_t (Obs.).	d_t (Calcd.).
900°	0·05	606 mm.	6·06	58·7	58·9
,,	0·05	433 ,,	3·54	58·9	58·5
,,	0·07	243 ,,	4·32	57·8	57·5
,,	0·12	99 ,,	5·69	55·0	54·5
1200°	0·34	950 ,,	497	46·0	46·3
,,	0·38	699 ,,	461	44·8	44·7
,,	0·48	412 ,,	489	41·7	41·9
,,	0·61	175 ,,	413	38·3	37·8

The values of the density are those relative to hydrogen as unit.

Not only may the density be re-calculated as indicated for the temperature for which K has been measured, but, with the assistance of equation (4) it can also be determined approximately for any other temperature and pressure, if the latent heat of transformation is known. The value of Q varies slightly with the temperature, but neglecting this, and inserting in the van't Hoff equation the value found at some lower temperature, K can be calculated for some higher or lower temperature. Thus, using the mean value of Q between 1100° and 1200°, namely,

* This equation is more often employed in the form

$$d_t = d_o + \frac{K'}{P} - \frac{K'}{P}\sqrt{1 + \frac{d_o P}{K'}} \text{ where } K' = \frac{Kd_o}{4}.$$

– 49,200 cal., the value of K at 1300° was determined and from it in turn the degree of dissociation (of P_4) which should occur at different pressures. At 1300°, these values are :—

P.	α.
1 atmos.	60 per cent
0·5 „	69 „ „
0·25 „	81 „ „
100 mm.	89 „ „

CHAPTER III.

THE MOLECULAR COMPLEXITY OF DISSOLVED SUBSTANCES.

THE extension, by van't Hoff, of the gas laws to solutions or to diluted matter in any form, makes it possible to determine the molecular weight of dissolved substances in a manner analogous to that employed for gases. The equation $PV = RT$ applies in common. For gaseous substances, the molecular weight is that quantity which occupies the gram-molecular volume at 0° and 760 mm. pressure, and is determined by a density measurement. For solutions, on the other hand, it is customary to start with a known concentration (or density) and find the osmotic pressure corresponding to it. This osmotic pressure may be determined directly or indirectly. So far, the indirect methods, depending on the measurement of freezing point, or vapour pressure reduction or boiling point elevation, are the ones of most importance in practice.

Raoult's empirical laws[2] would, however, enable molecular weight determinations to be carried out independently of the van't Hoff, or osmotic pressure, theory. For although these laws rest in theory on the laws of osmotic pressure, and it is sometimes convenient to calculate the molecular depression (C) of freezing point or elevation of boiling point from van't Hoff's equation, $C = \frac{0{\cdot}02T^2}{l}$ where T is the absolute temperature and l the latent heat of fusion or evaporation, yet in practice C is much more often determined by experiment, using some substance or substances generally accepted as normal. In this way the solvent employed is standardized.

Another method which is less often used is the partition coefficient method. If a substance is shaken with two immiscible solvents, each liquid appropriates a definite proportion of the whole such that if C_A is the concentration in solvent A and

C_B that in solvent B, then $\frac{C_A}{C_B}$ is a constant, independent of the total amount dissolved, provided the molecular complexity is the same in each solvent. If, however, association or dissociation occurs in one solvent, or in both but to different extents, then $\frac{C_A}{C_B}$ is no longer constant; but if the solute is normal in A and associated n times the normal size in B, the ratio

$$\frac{C_A{}^n}{C_B} \text{ or } \frac{C_A}{\sqrt[n]{C_B}}$$

is a constant quantity. From measurements of C_A and C_B, therefore, it is possible to determine the molecular complexity of a substance in one solvent relative to that in another. The process has been employed by Nernst, Hendrixson, Dawson, and Wedekind and Paschke.[54]

As the practice of the various methods is so well known, the results will be at once discussed.[55]

The Molecular State of the Elements.

(*a*) *Metallic Elements.*—Some of the earliest applications of the laws of Raoult were made with the view of extending them to metals. Thus we have the researches, in this field, of Heycock and Neville, Ramsay, and Tammann,[56] based, Ramsay's on vapour pressure, the others on freezing point measurements. The results obtained by Ramsay, who used mercury, and of Heycock and Neville who employed tin as solvent, are the more complete ones and will be the basis of consideration. The freezing point results are worked up so as to give, not the molecular weight, but the lowering produced by an atomic weight of the metal dissolved in 100 atoms of solvent.

Ramsay and Heycock and Neville came to the conclusion that most metals in metallic solvents have the simplest possible molecular constitution—monatomic. Heycock and Neville found that most of the metals produced much the same atomic lowering of freezing point in a given solvent, corresponding to Raoult's second law, and if, therefore, one metal could be regarded as monatomic then other metals, behaving similarly, must likewise be monatomic. This conclusion was very likely true because zinc and mercury in the state of vapour were known to be monatomic; and, further, from the van't Hoff

		Solvent—MERCURY.		*Solvent*—TIN.	
		VAPOUR PRESSURE RESULTS.		FREEZING POINT RESULTS.	
Element.	At. Wt.	Atoms of element per 100 Atoms Hg.	Mol. Weight.	Atoms of element per 100 Atoms Sn.	Atomic Lowering.
Lithium	6·9	1·70	7·1		
Sodium	23·0	0·86-5·35	21·6-15·1	1·317 - 4·73	2·82 -2·469
Potassium	39·1	1·55 and 5·26	29·1 and 30·2		
Copper	63·6			0·1388- 1·623	2·85 -2·798
Silver	107·9	3·22	112·4	0·099 - 3·705	2·96 -2·855
Gold	197·2	1·59 and 2·80	207·4 and 208·1	0·0663- 4·294	2·72 -2·89
Calcium	40·1	2·9	19·1	0·114 - 0·178	2·63 -2·24
Barium	137·4	0·90	75·7		
Magnesium	24·3	0·70 and 4·82	24·0 and 21·5	0·973 - 7·64	2·76 -2·846
Zinc	65·4	1·07-3·16	70·1-65·4	0·148 - 6·456	2·54 -2·489
Cadmium	112·4	0·75-3·51	100·2-103·8	0·0607-10·193	2·504-1·899
Aluminium	27·1	1·52 and 2·94	36·7 and 33·1	0·5 - 2·01	1·25 -1·363
Gallium	69·9	2·27	69·7		
Indium	114·8			0·1173- 0·495	2·24 -1·889
Thallium	204·0	0·81-3·33	163·6-197·6	0·112 - 7·97	3·09 -2·39
Tin	119·0	1·94 and 3·94	117·4 and 149·5		
Lead	207·1	2·00 and 4·39	199·9 and 250·2	0·0573- 0·4312	2·62 -2·794
Antimony	20·2	1·86-6·22	136·5-301·2		
Bismuth	08·0	3·77-4·68	214·5-232·2	0·0164- 4·02	2·44 -2·17
Manganese	154·9	1·14	55·5		
Nickel	258·7			0·098 - 0·2466	3·01 -2·717
Palladium	106·7			0·0308- 0·1863	2·28 -2·792
Mercury	200·6			0·0911-10·24	2·525-1·814

formula $C = \frac{0{\cdot}02\,T^2}{l}$, the atomic lowering C was calculated to be 3°, a value not very far from that obtained in a number of cases.

A few metals appear exceptional. Ramsay remarked that tin, lead, and bismuth have a tendency to become associated, whilst, from the freezing point measurements, aluminium may have a molecule Al_2. From the known tendency of the molecules of elements to increase in complexity as one passes from left to right in the Periodic Table (see p. 12) such association is possible in the case of these elements but there is little other ground for such a conclusion. As will be shown in the succeeding chapter, some of the abnormal results and deviations from the calculated freezing point depressions can be explained either on the ground of combination in solution, or by the formation and separation of solid solutions. Thus, the decreasing molecular weight values with increase of concentration found for sodium and potassium by Ramsay, Heycock and Neville and Tammann may be explained by formation of compounds.* By other

* See also footnote on p. 38.

methods, it has been found that combination occurs of mercury with sodium, potassium, and thallium [57]; of tin with aluminium and copper [58]; and of sodium with potassium, cadmium, thallium, lead and bismuth.[59] Solid solutions are also known to be formed between antimony and tin [60] and cadmium and mercury.[61] When these disturbing factors are taken into account, the general conclusion that metals in metallic solvents have monatomic molecules rests on very strong evidence.

(*b*) *Non-metallic Elements.*—Tests of the molecular state of these elements have not been numerous. Several gaseous elements, hydrogen, nitrogen, oxygen, appear to raise the freezing point of some solvents,* like benzene, possibly due to separation with the solid.[62] Iodine has been the subject of repeated investigation on account of its tendency to combine with certain types of solvent.[63] In neutral solvents, such as bromoform, it has a molecular weight near 254, corresponding to I_2.[64] Only phosphorus, sulphur, and selenium, so far investigated, have molecules greater than diatomic, the extent of the association being illustrated by the following values, in which the concentration C is expressed as grams per 100 grams of solvent.

Phosphorus [65] in Carbon Disulphide.

C.	M.W.
1·581	129
3·723	134
7·44	142
10·84	150
18·86	170

$P_4 = 124$

Sulphur [65] in Carbon Disulphide.

C.	M.W.
1·572	247
3·153	255
6·14	270
9·04	279
15·13	297
21·00	314

$S_8 = 256$

Selenium [66] in Phosphorus.

C.	M.W.
0·203	624
0·340	599
0·412	586
0·480	614

$Se_8 = 634$

Quite a number of investigators have busied themselves with the problem whether the various forms of solid sulphur exhibit different molecular weights in solution, but without finding any such difference.[67] As already stated, two types of molecule, S_8 and S_6, apparently exist in the vapour near the boiling point of the element. A study of the graphs on p. 18 for the vapour suggests that the amount of S_6 at such temperatures as those at which solution measurements are made will be very small, even in dilute solution (*see also* chap. VIII.).

* Solvents used in freezing point determinations are sometimes dried by passing through them a current of dry air, which usually has the effect of raising the freezing point.[119] In view of Garelli and Falciola's results, care ought to be taken in applying the method and, in any case, on account of the considerable solubility of gases in many organic liquids, the gas should finally be expelled from the solvent.

Once again, the only elements which are known to be associated, are those which tenant Groups V and VI of the Periodic Table, and this fact illustrates the close analogy between gases and solutions.

The Molecular Complexity of Compounds.

The study of the molecular state of compounds has brought to light many substances which exhibit molecular association. A table both of these compounds and of elementary substances, has been compiled as an appendix illustrating not only the variation of the molecular weight with the nature of the substance but also the effect of the solvent in very many cases. Many of the points raised in this and the succeeding chapter are illustrated in this table, making it unnecessary to introduce very complete illustrations in the text, so that it remains only to deal with the results in a general way.

It was found early in the study of the subject that associated substances admitted of ready classification. Associated organic substances, it was found, owe their condition to the presence of certain electro-negative groups. Such groups are the OH, COOH, CONH, NOH, CN, SH, CSNH, CSOH, NH_2, NO, CHO, CO, and CS, conferring the power of association on alcohols, phenols, carboxylic acids, amides and anilides, oximes, nitriles, mercaptans, thioacids and amides, primary amines, nitroso compounds, aldehydes and ketones. The Appendix contains numerous illustrations of such substances. Solution measurements, therefore, have very greatly enlarged our knowledge of molecular association, as, with the exception of acetic acid, no organic substances are definitely known to be associated in the state of vapour.*

Among the first inorganic compounds to be recognized as associated were the oxides nitrogen peroxide,[68] phosphorous oxide in benzene[69] and arsenious oxide in nitrobenzene.[70] More recently hydrogen chloride and nitric acid and a large number of salts have been added to the list. In the author's view, electrolytes as a class are associated substances, and some evidence of this will be forthcoming in a later chapter.

Dealing now with the substances in three divisions we have :—

* Schulze[67a] concludes from his experiments that carbon disulphide and nitrobenzene are slightly associated in the vapour state,

A. Organic Compounds, Excluding Salts.

The examples are numerous. It does not follow that one of the electro-negative groups already mentioned confers the power of forming aggregation on the substance without relation to the rest of the molecule. The majority of associated substances contain an electro-negative group united to some hydrocarbon radicle, and as hydrocarbons as a class have no tendency to association, we may expect hydrocarbon radicles to have a normalizing tendency, its extent depending on their mass. Hence, it follows that as a series of homologous substances is ascended, the degree of association diminishes and is ultimately reduced to zero. Thus, methyl and ethyl alcohols, formic and acetic acids, formamide and acetamide are the most strongly associated of their class.[71]

Of the groups causing association, some exert a powerful, others only a weak influence. Thus, from the Appendix it will be found that the class of compounds in which the highest degree of aggregation is reached is the alcohols; then follow amides, carboxylic acids, oximes, and anilides. To the oxygen atom must be ascribed considerable power of producing association, for when replaced by sulphur, the analogous compounds containing the groups SH, CSNH, and CS are but slightly associated.[72] Then, again, the groups CHO and CO have also only a weak influence; for whereas acetone is slightly associated in benzene solution, acetylacetone and most other ketones are normal.[73] Benzaldehyde and its derivatives are likewise normal.[74] A number of general rules may be formulated in connexion with the association of organic compounds, and a short statement of the important ones will assist the reader in a survey of the subject.

1. The tendency to association in organic compounds is connected with the presence of certain electronegative groups, OH, CONH, COOH, NOH, CN, SH, CSNH, CSOH, NH_2, NO, CHO, CO, CS, their influence decreasing in the order given.

2. The degree of association depends also on the mass of the molecule, diminishing as the formula weight increases. This applies both to aliphatic and aromatic compounds.

3. With aromatic substances, the ortho-substituted compound is least and the para-compound most associated.[75]

4. The degree of association depends also on the presence of

other groupings in the molecule. Thus, the groups acting as substituents in a molecule, as in the phenols, exert a normalizing tendency as follows :—

$$CH_3 > Cl > Br > I > NO_2 > CO_2R.$$[75]

5. The degree of association depends on the structure of the molecule. Thus, primary alcohols are most and tertiary alcohols least associated.[76]

6. The degree of association depends on the solvent (chap. IV.).

B. Salts.

By far the most systematic comparison of salts has been carried out with those derived from organic ammonium, sulphonium and oxonium bases, as these dissolve in a wide range of solvents much more readily than metallic salts. Strong association has been found with all true salts, the degree of association being, on the whole, considerably greater than with non-electrolytes. Thus, in chloroform, tetraethylammonium bromide may have, according to the concentration, a degree of association greater than eight, and triethylsulphonium iodide of twelve. The actual degree of association depends on a number of factors,[77]

1. *On the base.*—As a rule, the degree of association of similarly constituted salts decreases as the mass of the base increases. Thus, the association decreases in the order monoalkyl-, dialkyl-, trialkylammonium chlorides; dimethyl-, diethyl-, and dipropylammonium chlorides; tetraethyl- and tetrapropylammonium chlorides. But mere mass is not the controlling factor, and structure must play a considerable part; for, instead of a decrease in the degree of association being found on passing from the trialkyl- to the tetraalkylammonium salts, an increase occurs; likewise, the quaternary compound, quinoline ethiodide, is more associated than quinoline hydriodide.

So far as the alkylammonium and alkylsulphonium bases are comparable, the salts of nitrogen bases are the more strongly associated.

2. *On the acid.*—Of the halogen salts, chlorides appear least and iodides most strongly associated, so that the degree of association does not fall, here, but rises with increase in mass. Indeed, with periodides,[78] the extent of complexity appears to be

still greater than with iodides. Nitrates[77] are likewise strongly associated, in chloroform slightly more than iodides.*

3. *On the solvent*, the *concentration* and the *temperature* (see below).

For metallic salts, very similar rules hold,[78] the degree of association falling with rise of atomic weight for compounds of allied elements, whilst the chloride is also least and the iodide most associated of the haloid salts, as in the lithium compounds.

The tendency to molecular association shown by inorganic substances appears to be connected with the relative positions of the component elements in the Periodic Table. Nitrogen peroxide, phosphorous oxide and arsenious oxide are compounds of oxygen and elements in Group V. All of them are non-electrolytes, though, as anhydrides, they can readily produce electrolytes by the addition of water. The electrolytes are strongly associated, as hydrogen chloride, which is strongly associated in benzene and nitrobenzene,[119] and so also are salts. The essential difference in the behaviour of electrolytes and non-electrolytes is illustrated in the compounds of the halogens with Group V elements. Thus phosphorus and arsenic tri-chlorides are non-associated, but antimony trichloride exhibits quite distinct association. The evidence indicates that as we pass from left to right in the Periodic Table, the power of the haloid compounds of the elements to form molecular aggregates diminishes.[79]

Solid Solutions.

In the region of solid solutions the most available method is the application of the Partition Law. So far as the discovery of association, or any abnormal molecular complexity is concerned, the results are as yet very meagre. One of the most interesting cases concerns the absorption of gases in solid materials. When hydrogen diffuses through palladium[80] or through iron,[81] or dissolves in palladium,[82] or nickel,[83] it does so to an extent which is proportional to the square root of the pressure. There are two possible ways of explaining such a result, either that Henry's Law in regard to the solubility of gases (namely, that $\frac{C_1}{C_2}$ shall be constant, where C_1 measures the concentration (pressure) of

* Fluorides, chlorates, bromates, iodates, and sulphates have also been found, from measurements in the author's laboratory, to be associated strongly.

the gas outside the absorbing medium and C_2 that within the medium), does not apply to such cases of absorption; or, that the gas must diffuse in the atomic state, when $\frac{\sqrt{C}}{C_2}$ should be constant. One difficulty in the way of the second explanation lies in the fact that the absorption of carbon dioxide in charcoal [84] is also expressed by the relation $\frac{x}{\sqrt[3]{P}}$, from which it might also be concluded that the carbon dioxide molecule was dissociated into three parts during the process of absorption. Such an explanation for carbon dioxide is not thinkable. It is now generally recognized that for most gases, Henry's Law does not apply to their absorption by solids, but that in at least one case, hydrogen in charcoal, there are two processes, the first a rapid absorption to which Henry's Law does not apply, the second a very slow process of true solution. According to McBain,[85] the second process of true solution occurs at a rate proportional to the square root of the pressure, and the only conclusion to be drawn here is that the hydrogen suffers a dissociation, diffusing inwards in the atomic condition. Not only is this conclusion drawn for solid solution, but also for solutions of hydrogen in molten copper and of oxygen in silver and in gold-silver alloys.[86] Sieverts and Hagenacker suggest that such dissociation into the atomic condition may be occasioned by the monatomic molecules of the metal in some way. Such an explanation cannot be applied, however, to solution in charcoal.

Solutions of solids in solids so far investigated, include no case in which the degree of association has been measured. If a solute is associated in a given solvent and separates with the solid solvent in a manner governed by Henry's Law, then the conclusion may be drawn that it is associated to the same extent both in the liquid and solid solutions. Probable examples are furnished by antimony and bismuth bromides in aluminium bromide,[87] but the partition coefficient between liquid and solid has not been satisfactorily determined in these cases.

Colloidal Solutions.

Colloids furnish another and very interesting type of association. They are substances which possess a very big molecular weight, as all results indicate. Thus, Pfeffer found that a solution

of gum arabic in water, at 15°, exerted but a small osmotic pressure, the values of the molecular weight calculated from the osmotic pressure ranging from 2570 to 4110,[88] but obviously without any great degree of accuracy.

Freezing point measurements lead to very similar results. In water, quite a number of cases have been tested, of which the following table includes a selection :—

Substance.	Concentration.	M.W.
White of egg [89]	14·5-44·5	14,000
Maltodextrin	10·0	6500
Starch [90]	?	25,000
Gum arabic	14·0	1612
Caramel	8·76 - 22·5	1585-1745
Ferric hydroxide [91]	1·16 - 2·60	5452-4888
Aluminium hydroxide	0·523 - 1·37	410-1073
Tungstic acid [92]	1·2 - 100	679- 995
Silicic acid [93]	—	800-1600

The objection to freezing point measurements is the possible influence of small quantities of salts or other impurities which, on account of the adsorptive power of colloids, it is difficult to remove ; and the question has been raised whether colloidal substances of themselves can exert an osmotic pressure. Despite certain evidence that no osmotic pressure is exerted,[94] it can be safely concluded from the work of Linebarger, Lillie, Moore and Roaf,[95] and others that a definite though small osmotic pressure is set up, corresponding to a high molecular weight.[96]

Although the investigation of the conditions of the formation of colloidal solutions is far from complete, there are certain resemblances between ordinary association and colloidal solutions which may be indicated. In the first place, the gas laws and laws of distribution which apply to substances in ordinary solution, whether associated or not, have more recently been shown to be equally valid for colloidal substances.[97] We may in fact regard the formation of colloidal solutions as a limiting case of association, and it is quite possible that the upper limit of the degree of association of, for example, salts, would be found in a colloidal solution. Already, from measurements made in chloroform, the molecular weight values for some salts run up to numbers which one is accustomed to connect with colloidal substances as, for example, tetraethylammonium bromide which reaches (not as a limit) a value exceeding 1800, or of triethylsulphonium iodide exceeding 2500.[98] Then again, the

influence of the solvent, in a very general way, is the same in both cases. It has been pointed out elsewhere, that association of a substance occurs as a rule in solvents in which the substance is but little soluble. This applies also to colloidal solutions, for colloids are produced in solvents in which true solution is not formed. Thus, ordinary soluble salts are looked on as crystalloids in regard to aqueous solution. At any rate they do not form colloidal solutions in water* but can do so in organic liquids in which they are insoluble in the ordinary sense. Arsenious and antimonious sulphides which are insoluble in water, are associated in the sense of forming colloids, in this medium. What the effect of a series of solvents is on the size of colloid particles cannot be said. Organic substances can form colloidal solutions in media other than water, as, for example, caoutchouc in benzene[100] and casein and starch in formamide.[101]

The effect of temperature increase is also to reduce the size of colloidal particles.[102] One further factor, the influence of added electrolytes is, on the other hand, to increase the size of the colloidal particle, or to diminish it according to the character of the ions added, before precipitation occurs, as has been proved by Biltz and Vegesack, and Mayer, Schaefer and Terroine.[103] Little is known of any similar phenomenon connected with ordinary association, but the recently demonstrated effect of one salt increasing the degree of association of a second in solution,[104] may, at any rate in the early stage of the action, have something in common with the effect of electrolytes on colloids.

The Influence of Temperature on Molecular Weight.

The range of temperature over which it is possible to study the molecular weight of a substance in solution is in most cases much more limited than with a gas. Arguing from the analogy between the two states, it would be expected that rise of temperature should bring about a reduction in the degree of association of a substance, and so far as tests have been made this actually is the case. With a solution, however, it must be clearly borne in mind that other factors have to be considered. Thus, a very important influence is exerted by the dielectric constant of the solvent, and the value of this property decreases with rise of temperature,

* Unless they are protected by a coating of a natural colloid as in the case of silver chloride.[99]

tending, therefore, to maintain the associated condition.[105] To ascertain the true effect of temperature, therefore, a knowledge of the temperature variation of other factors is obviously essential.

There are several ways in which the influence of temperature may be studied. The first is to make determinations of the molecular weight by freezing point and boiling point methods for a given solvent. Thus we have the following values derived in this way, the concentration being, for benzoic acid in benzene, 25 milligram molecules per 100 grams of solvent; for tetraethylammonium bromide, 25 milligram molecules per 100 c.c. of solvent.

BENZOIC ACID IN BENZENE.[106]

$t°$	M.W.
5·5°	233
80°	193

TETRAETHYLAMMONIUM BROMIDE IN ACETIC ACID.[107]

16·6°	527
118°	337

A more thorough test was that made by Innes[108] on the degree of association of several organic substances, namely, benzoic and o-bromobenzoic acids, β-benzilmonoxime and dimethyltartrate in the solvent benzene, which was made to boil at a series of temperatures by varying the external pressure. A series of measurements was first carried out with normal substances in order to deduce the molecular elevation of boiling point at each temperature. Fig. 4 records graphically the results with benzoic acid and it will be seen that with rise of temperature there is a steady fall in the molecular complexity for any given concentration. The curve for 93° lies above that at 80° and in its upper portion cuts the curve for 73°, but the known volatility of benzoic acid below its melting point may account for this. The other substances tested gave results of similar character.

As already mentioned, other factors, the variation of the dielectric constant must be remembered. In the case of benzene this variation is, however, very small.*

The heat of association or dissociation must be a factor determining the stability of the molecular complexes. Its actual value could be determined, as with gases, if the precise effect of temperature on the degree of association were known.[108]

* As yet unpublished result.

The Effect of Concentration.

As already seen in chapter II. cases of molecular association follow, in the simplest case, the equation :—

$$A_n \rightleftarrows nA$$

and must be influenced, accordingly, by the pressure or molecular concentration in such a way that increase of concentration brings about an increase in the degree of association. Where experiment proves that the reverse occurs, namely, decrease with increasing concentration, it can with considerable assurance be concluded that chemical combination occurs between solvent and solute.

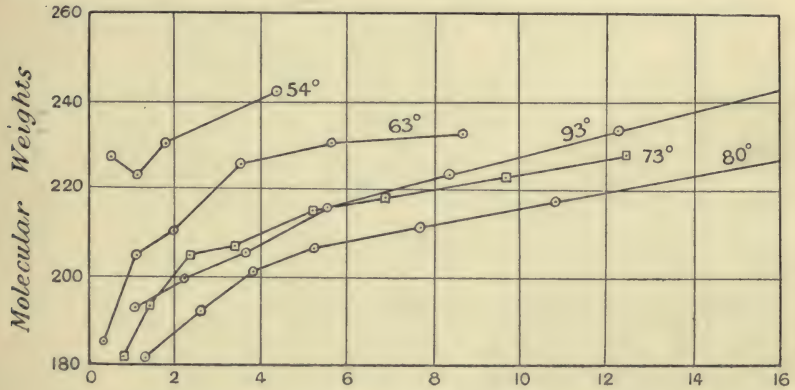

FIG. 4.

Fig. 5 indicates for some typical cases the manner in which the molecular weight varies with concentration. In general, a particular form of curve is representative of a class. Thus, Auwers [109] found that the alcohols have nearly straight line curves, rising rather steeply, and so have the phenols, amides, and anilides. Salts also generally follow this type.[110] Benzoic and similar aromatic acids are strongly associated even in dilute solution, and after rising steeply for a short distance, the curve rapidly changes in direction and its slope becomes quite small.

The slope of the curve will obviously depend on the limiting value of n in the complex A_n. Auwers was led to divide associated substances into two classes on the basis of this difference in the type of curve, the first class comprising the aromatic acids, in which there appeared from his measurements to be an upper

limit of $n = 2$, the second class containing substances in which the molecular weight increases proportionately to the concentration. Most substances belong to this second class, alcohols, phenols, aliphatic acids and salts. Views have been expressed that some salts have an upper limit to the degree of association. Thus, Hantzsch and Hofmann [111] believed that tetraalkylammonium salts in chloroform behave very simply, the molecular state being nearly independent of the concentration and having a degree of association of five as an upper limit; whilst Wedekind

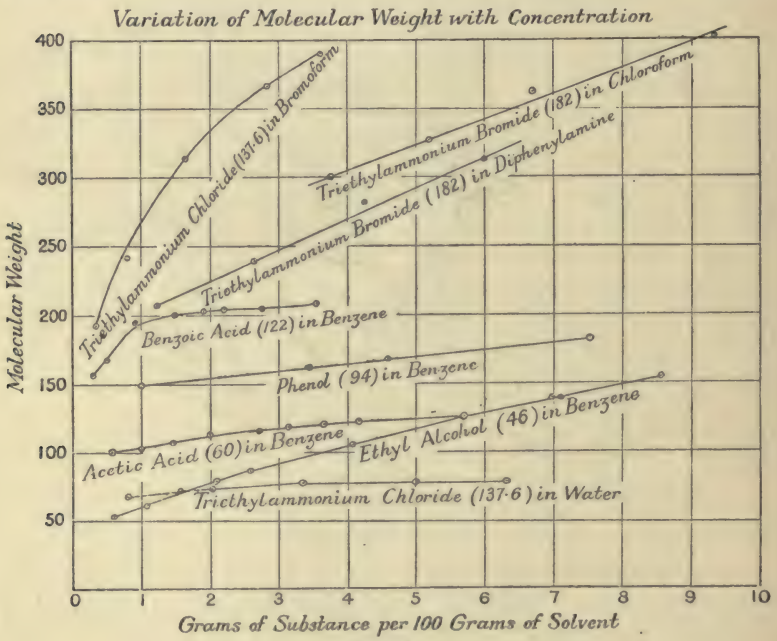

FIG. 5.

and Paschke [112] regarded salts as having an association factor of 2. Both deductions were made from insufficient data, for, to quote but one example, tetraethylammonium bromide in a 9 per cent solution in chloroform has a degree of association of 9. Certain salts appear unaffected by alteration of concentration, but the molecular weight found in such cases is often nowhere near a multiple of the simple molecular weight.[113]

What the upper limit of complexity may be in the case of substances which at moderate concentrations have straight line curves connecting molecular weight and concentration is rather

an interesting speculation. The ordinary methods available for dilute solutions could not be applied.

When we come to deal with the lower limit of association we are on surer ground. Continuous reduction of pressure on a gas tends to reduce the molecular state to the simplest possible, and in like manner, decrease of concentration should bring about a similar state in solution. As will be seen from Fig. 5, there are one or two cases in which expectation is fulfilled, for example, ethyl alcohol in benzene. On the other hand, the production backwards of several of the curves would not lead to intersection of the y axis at the normal value of the molecular weight. Probably, however, the direction of the curve for very dilute solutions alters as the concentration increases.

The quantitative study of the relation between concentration and degree of association has, however, made but little progress. On the basis of the Law of Mass Action, assuming a direct change into single molecules on dissociation, the state of equilibrium $A_n \rightleftarrows nA$ must be expressible by the equation

$$K = \frac{C_A{}^n}{C_{An}}$$

where C_A and C_{A_n} are the respective concentrations of single and complex molecules. Nitrogen peroxide in chloroform solution, affords the only satisfactory example of an associated substance which dissociates in solution according to the requirements of the Law of Mass Action.[113a]

The resemblance between the curves representing the dissociation of benzoic acid in benzene and of weak electrolytes in water led Auwers [114] to apply the equation to substances of the first class, namely, aromatic acids, for here, presumably, the limits are simple, varying from $n = 1$ to $n = 2$. The equation then becomes

$$c = K \frac{1 - y}{y^2}$$

in which c represents the concentration, y the degree of dissociation of the double molecule and K the equilibrium constant.

If, therefore, in a solution of unit molecular concentration, calculated on the basis of the single molecule, e represents the number of single molecules, d the number of double ones, then

$$e = 1 - 2d \text{ or } d = \frac{1 - e}{2}.$$

But the lowering of freezing point and the number of molecules are so connected that

$$\frac{m}{M} = e + d$$

from which

$$d = \frac{M - m}{M}, \text{ and } e = \frac{2m - M}{M}.$$

Further, $$y = e = 1 - 2d = \frac{2m - M}{M}.$$

Substituting these values in the simple mass action formula, we get,

$$K = c\,\frac{(2m - M)^2}{2M\,(M - m)}.$$

This formula was applied to various cases of association but only found to be in any way satisfactory in very few cases, as with benzoic acid in benzene and o-bromobenzoic acid in naphthalene, for which the following values were calculated :—

Benzoic Acid ($m = 122$).			o-Bromobenzoic Acid ($m = 201$)		
C.	M.	K.	C.	M.	K.
0·268	219	0·0039	0·29	269	0·14
0·567	223	·0056	0·78	293	0·17
1·444	228	·0076	1·56	311	0·19
2·603	232	·0073	3·05	332	0·17
4·725	236	·0056	4·51	340	0·18

For most acids as well as oximes and members of the second class, the values of K decreased throughout with increasing concentration, and even the aromatic acids only gave satisfactory results when the concentration did not exceed 4 centigram molecules per 100 grams of solvent. The phenomenon of association in solution is evidently not simple. Possibly some of the factors which cause strong electrolytes in aqueous solution to disobey the Law of Mass Action also operate in complicating the process of association. It is quite possible that the assumption of an upper limit of 2 for the degree of association is not correct and that more than two types of molecule may be present, in which case each dissociation will be marked by a distinct equilibrium constant. Auwers himself suggested the cause of the disturbance to be some reaction between solvent and solute, an idea which he proceeded to test by investigations on the influence of the chemical constitution of the solvent, an influence which he found quite as powerful as the nature of the solute itself. The whole subject of this influence will be dealt with in a general way in the succeeding chapter.

CHAPTER IV.

THE MOLECULAR COMPLEXITY OF DISSOLVED SUBSTANCES.

The Influence of the Solvent.

So far in our study of molecular association, the known analogies which exist between the gaseous state and solution have been of considerable assistance; but now new factors must be taken into account. For although it is interesting to liken a gas to a solution in the ether (assuming the existence of the ether), little is known of such a medium beyond its power of conveying energy. In the measurement of gas densities no second substance is present, except in the methods of Meyer and of Lumsden; but here the only effect which the filling gas exerts is due to its action as a diluent, bringing about somewhat increased dissociation, where dissociation can occur at all, to an extent depending on the extent of admixture with the vapour. In any case, the filling gas is so chosen that chemical action is rigidly excluded.

In a liquid solution, however, the solvent plays an important part. Its action may be wholly physical, or partly also chemical. The effect of chemical action will be considered first.

I. Combination between Solvent and Solute.

At first sight, there are two possible ways in which the observed molecular weight of a substance may be affected by combination in solution. On the one hand it may be argued that the compound formed will make its presence known in an increased molecular weight, the value found being due partly to uncombined solute and partly to the compound; on the other hand, the action may be regarded as merely reducing the amount of free solvent, thereby concentrating the solution and leading to a lower molecular weight, since the osmotic pressure, depression of freezing-point, or vapour pressure, will be thereby increased. Ramsay,[115] in his study of metallic solutions, took the former

view; the result of experiment, however, may be said to prove the correctness of the second.

The proof of the reduced value in the molecular weight observed when combination occurs lies in the study of cases in which combination is known to occur.* It has recently been pointed [116] out that, although the general effect of combination is always to make the observed molecular weight lower than it would be in the absence of such combination, there are five ways in which the molecular weight may vary with concentration, supposing molecular association and combination both to exist.

1. *The molecular weight decreases with increasing concentration.*—Benzoic acid in *p*-toluidine,[117] for example, where combination occurs, illustrates this case. Another example, of a different type, is that of lithium chloride in ethyl alcohol.[118] These two substances combine to form LiCl, $4C_2H_6O$. The variation of the molecular weight is as below, C indicating the number of grams of the salt dissolved in 100 grams of the alcohol:—

C.	M.W.	
2·244	34·0	
2·655	33·0	LiCl = 42·5
3·406	30·1	
4·075	29·2	

Hydrogen chloride, both in benzene and in nitrobenzene, is strongly associated, but as the concentration increases, the apparent degree of complexity falls off, a fact only to be explained by the occurrence of chemical combination.[119]

2. *The molecular weight increases with increasing concentration.*—Here, despite combination, the rate of increase of complexity is greater than the reducing effect due to combination. Several examples occur in the determinations of Werner, such as in the case of cadmium bromide in piperidine.[120]

3. *The molecular weight increases to a maximum and then falls.*—Such a phenomenon will be observed in cases where there is a rapid increase in the degree of association in the early stages

* Neglect to take into account the heat of dilution introduces the same kind of an error as is now discussed under the head of chemical combination. Thus, when the heat of dilution is taken into account, the molecular weights of sodium and potassium in mercury (p. 23) have normal values. It is probable, however, that in most cases where it is necessary to correct the osmotic pressure (freezing-point, etc.), for heat of dilution, that chemical action between solute and solvent occurs; so that a chemical explanation can, in fact, be offered for an abnormal physical property.

For a discussion of the effect of heat of dilution see Findlay's "Monograph on Osmotic Pressure" in this series.

(that is, while the solution is still dilute) since the effect of combination only becomes pronounced in concentrated solution. Quite a number of examples may be quoted; indeed, this type seems by far the commonest. Lithium iodide in amyl alcohol, from which, at lower temperatures LiI, $4C_5H_{12}O$ can be isolated, and potassium iodide in liquid sulphur dioxide, where combination to form $KI.4SO_2$ occurs, may serve as examples. C represents grams of solute per 100 grams of solvent.

Lithium Iodide in Amyl Alcohol.[118]		Potassium Iodide in Sulphur Dioxide.[121]	
C.	M.W.	C.	M.W.
1·777	154·4	0·371	282
4·125	159·2	0·735	331
8·053	151·2	1·13	352
11·97	151·5	1·58	288
		2·05	289
		2·46	222

Other examples are furnished by lithium bromide and iodide in butyl alcohol and lithium bromide in amyl alcohol, where compounds of the type LiBr, 4ROH are formed;[118] by potassium iodide in iodine,[122] and probably a variety of salts in *p*-toluidine.[105]

The possibility of the two other cases follows from the three already given, so that it is quite possible to have (4) the molecular weight remaining constant over a certain range of concentration, the increase of association being counterbalanced by the effect of combination, and (5) the molecular weight falling to a minimum value.

The fact to be borne in mind is that combination in solution has the effect of reducing the molecular weight. Further evidence, beyond that given, is that where combination does not take place, the molecular weight of an associated substance increases steadily with the concentration, as with lithium nitrate in ethyl, *iso*-butyl, and *iso*-amyl alcohols, where no compounds are formed.[118]

II. The Physical Influence of the Solvent.

A. *Separation of the Solute with the Solvent.*—This is a factor which is apt to cause confusion, when not understood, and to lead to the idea either that a non-associated substance is associated or that the degree of association is greater than is actually the case. For if the solute separates in any manner with the solvent, the solution remaining is more dilute than if no separation occurred. In consequence, the osmotic pressure, as measured by

freezing point or vapour pressure determinations, is reduced and the apparent molecular weight is high. Such separation can occur either by the formation of solid solutions or by the volatility of the solute in a boiling point or vapour pressure determination.

An interesting example is furnished by iodine in benzene. On other grounds there is no evidence that this element is associated (*cp.* p. 24), but cryoscopic determinations in benzene lead to molecular weights between 350 and 360, whereas $I_2 = 254$. The explanation was forthcoming when Beckmann and Stock [123] found that iodine forms a solid solution in benzene.

If the extent to which a substance separates with the solvent is determined this amount can be allowed for and the true amount in solution deduced. Supposing that a is the fraction of the substance in the solid solution or in the mixed vapours, then the concentration of the liquid solution will be reduced to $C(1 - a)$, where C was the original concentration. Therefore the usual equation for the calculation of molecular weight becomes:—

$$M = \frac{C\,(1 - a)\,K}{\cdot \Delta^{\circ} W}$$, where K is the elevation or depression constant, Δ° the observed rise of boiling point or fall of freezing point and W the weight of solvent. The quantity a corresponds to the partition co-efficient, and can be determined by a method such as that of Bijlert,[124] for solid solutions. The determination of a in the vapour state is less easy. If the solute is an acid, however, the vapour arising from the solution can be distilled over and analysed.[125]

As an indication of the extent of error involved by the separation of solute with the solvent, the behaviour of thiophene in benzene may be quoted.[126]

C.	M.W.
0·51	133
1·12	133
2·16	133
3·25	134

When correction was made for the amount of thiophene freezing out with the benzene, the mean molecular weight observed became 78·1 as compared with the calculated value of 83·8. When a non-associated solute separates with the solvent, therefore, the observed molecular weight is higher than the normal, but is independent of the concentration. The degree of com-

plexity of an associated substance is, as already indicated, dependent on the concentration.

How many of the cases of actual association are subject to an error due to separation with the solvent is quite unknown, as it is seldom that the nature of the solid separating out is tested. Acetic and benzoic acids and *a*-benzaldoxime in benzene certainly are not.[126] Benzoic and a number of aromatic acids do separate with water vapour at the boiling-point of the solvent,[125] and antimony and bismuth bromides in aluminium bromide are further examples of associated substances which separate with the solvent, in this case on freezing.[87]

B. *Dielectric Constant of the Solvent and Other Physical Actions.*—The power of forming complex molecules in solution appears to depend in a very great measure on the solvent apart from any chemical action. Raoult and the early workers in the same field found that the association of organic substances containing the hydroxyl group was exhibited when the solvent was a hydrocarbon or a halogen or nitro-derivative of a hydrocarbon, and all subsequent work substantially proves this regularity.

The first systematic researches on the influence of the solvent were made by Auwers who studied the effect of the chemical constitution both of the solute and the solvent on the degree of association, finally coming to the conclusion that the influence of substituent groups could be set out in a regular manner, in the order

OH, COOH, NH_2, CHO, CN, COOR, NO_2, I, Br, Cl.

When these groups are present in the molecule of a solute, the most abnormal result is obtained when the OH group is present, and least with Cl ; when present in the solvent, the OH group has the greatest normalizing effect (that is, is most effective in reducing the molecular weight of a solute to the normal) and Cl least. This rule was put forward as expressing in a general manner the results obtained without being claimed as applying universally.[75] Certain possible physical influences were tested, such as the melting-point and the molecular freezing-point depression of a given solvent, but were found to be without effect.

It is quite possible, however, to refer the molecular complexity more or less successfully, according as the solute is an electrolyte or a non-electrolyte, to the dielectric character of the

solvent. Already, in 1893, J. J. Thomson [127] had put forward the hypothesis that "if the forces which hold the molecule together are electrical in their origin, . . . these forces will be very much diminished when the molecule . . . is surrounded by a substance possessing a very large specific inductive capacity". This reference, although in a paper on the conduction of electricity through gases, suggested a connexion between dissociation in aqueous solution and the specific inductive capacity of the solvent. Shortly afterwards Nernst,[128] again on the assumption that chemical forces are electrical in their origin, added the statement in regard to association "Wir werden erwarten können, dass Lösungsmittel um so stärker Doppelmoleküle zu spalten vermögen, d. h. eine um so grössere dissocierende Kraft besitzen, je grösser ihre D. E.* ist. Dies bestätigt sich volkommen". Nernst referred to rather different substances from Thomson, for the association of salts was not then known. The reference, in particular, was to organic acids, which are associated in benzene, a solvent of low dielectric constant. The combined statement of Thomson and Nernst is known as the Nernst-Thomson hypothesis, and until the last few years had been confined in its application to the ionization of electrolytes.

It is not difficult to show that Auwers' results can be referred fairly successfully to the dielectric constant of the solvent. As already stated the normalizing effect of different groups contained in a solvent decreases in the order

OH, COOH, NH_2, CHO, CN (COOR), NO_2, I, Br, Cl.

Now the dielectric constant of a solvent is likewise affected, in general, by the nature of the groups present. According to Walden,[129] decrease in the dielectric constant occurs as substitution proceeds in the order from left to right,

OH, NO_2 (CO), CHO, COOH, CN, NH_2, F, Cl, Br, I.

The order is not quite the same in the two cases, the NO_2, COOH, and NH_2 groups being in different positions; but as the effect of the halogens on the dielectric constant may also be in the reverse order to that given, there is a similarity between the two arrangements.

The effect of the dielectric constant can be better illustrated by reference to the actual numbers obtained. Weak electrolytes, benzoic acid, and acetic acid, and a non-electrolyte, formanilide,

* The symbols D. E. refer to the dielectric constant.

will be first considered. In the following table the original results, drawn from a large number of sources, have been collected and recalculated to a common concentration, namely, a solution containing 30 milligram molecules of the solute (assuming the simple formula for the calculation) per 100 c.c. of the solvent. M_{30} gives the molecular weight at this concentration. K_t represents the value of the dielectric constant at the temperature $t°$, as near as possible to the temperature of the determination.

Solvent.	K_t.	M_{30}.		
		Benzoic Acid (122).	Acetic Acid (60).	Formanilide (121).
Water	$66_{100°}$	* (240) [125]	58 [138]	157 [143]
Ethylene cyanide	$61{\cdot}2_{60°}$	180 [130]	—	—
Nitrobenzene	$40{\cdot}0_{6°}$	280 [119]	(associated) [139]	—
m-Dinitrobenzene	$20{\cdot}6_{90°}$	167 [75]	—	—
p-Nitrotoluene	$18{\cdot}4_{52°}$	—	—	157 [75]
Ethyl alcohol	$18{\cdot}0_{78°}$	125 [131]	—	117 [143]
Acetone	$17{\cdot}0_{56°}$	119 [131]	—	120 [143]
Sulphur dioxide	$14{\cdot}0_{20°}$	222 [132]	94·6 [132]	—
Phenol	$9{\cdot}7_{48°}$	133 [133]	—	—
Acetic acid	$6{\cdot}3_{18°}$	129 [134]	—	—
p-Toluidine	$5{\cdot}4_{43°}$	142 [117]	—	128·5 [75]
p-Bromotoluene	$5{\cdot}07_{28°}$	—	106 [140]	
Ethylene dibromide	$4{\cdot}86_{18°}$	—	118 [139]	—
p-Dibromobenzene	$4{\cdot}57_{85°}$	230 [75]	—	—
Bromoform	$4{\cdot}3_{7{\cdot}5°}$	—	121·8 [141]	—
p-Methyl toluate	$4{\cdot}28_{33°}$	166 [75]	—	149 [75]
Chloroform	$4{\cdot}13_{61{\cdot}2}$	214 [131]	—	160 [143]
Ether	$4{\cdot}12_{35°}$	126 [131]	—	164 [143]
Naphthalene	$3{\cdot}2_{80°}$	212 [136]	—	—
Nitrogen peroxide	2·5	210 [135]	(120) [142]	—
Carbon disulphide	$2{\cdot}5_{46°}$	243 [131]	—	—
Benzene	$2{\cdot}3_{5{\cdot}5°}$	236 [134]	117 [134]	213 [143]
p-Xylene	$2{\cdot}15_{18{\cdot}2}$	—	—	244 [75]
Cyclohexane	2·07	>230 [137]	135 [137]	—

The view of Nernst, based on a very limited number of results, and of Meldrum and the writer,[144] from more extensive measurements on amides and anilides, was that the dielectric constant of the solvent was probably the controlling factor on association. This conclusion, in the case of the substances selected as examples in the above table, requires some modification, and further investigation. It is true that in solvents of low dielectric constant, association almost always

* This is the value at the concentration 50 milligram molecules per 100 c.c. of solvent.

occurs. Ether as a solvent for benzoic acid is obviously an exception, although it falls into line when formanilide is the solute, and the low value with p-toluidine can, in the case of benzoic acid, be referred to chemical action (*vide* p. 38). But, although association is almost general in solvents of low dielectric constant, it is far from absent when the dielectric constant is high. Thus, pronounced association occurs with benzoic acid in water, ethylene cyanide, nitrobenzene and m-dinitrobenzene, whilst formanilide is associated in water and p-nitrotoluene. It must be conceded that although the dielectric constant undoubtedly plays a distinct part, it is not the controlling factor with all organic associated substances. The influence of the chemical nature of the solute is evident in the three examples chosen, and it appears that there is a distinct difference between aliphatic and aromatic compounds. Acetic acid, so far as has been tested, is much more influenced by the dielectric constant than benzoic acid and formanilide, which contain the benzene nucleus. The examples quoted in the Appendix add further evidence of this fact.

The existence of molecular complexes in aqueous solution is hardly to be looked for on the usual view of the dissociating effect of water, but such is actually the case. A number of organic acids and phenols,[145] amides and anilides[146] appear to be strongly associated in water as well as in the so-called *associating solvents*, a term whose application becomes difficult in view of the effect of water as a solvent. The occurrence of molecular association in water is of interest and importance from other points of view, however, for in practically all cases, the more strongly associated the substance in benzene and solvents of low dielectric constant, the less the substance is associated in water, and vice versa.[146] A few examples will make this clear, the association factors referred to being deduced for a common concentration of 50 milligram molecules per 100 c.c. of solvent.

Substance.	Association Factor. Water.	Benzene.
Propionamide	1·14	2·03
n-Butyramide	1·12	1·98
iso-Butyramide	1·18	1·94
Valeramide	1·22	1·82
iso-Butylacetamide	1·50	1·79
Methylacetanilide	3·00	1·04

Substance.	Association Factor. Water.	Benzene.
Benzoic acid	1·98	1·97
o-Hydroxybenzoic acid	1·70	—
m- ,, ,,	1·23	—
p- ,, ,,	1·14	—
Phenol	1·13	1·89
p-Nitrophenol	1·46	1·38

The hydroxy-acids quoted are not sufficiently soluble in benzene to be tested, but from tests in naphthalene it appears that the usual rule of the para- compound being most associated and the ortho- least is adhered to. The inversion of the order for benzene and water is very clear. Once more the strong effect of the benzene nucleus in producing association in spite of the solvent is brought out.

On the basis of the regularity demonstrated, the suggestion has been made that possibly the association in water is only apparent, and that in reality it is due to the dissociation of the water molecules, which are known to be complex [145, 146]. A number of other observers, Robertson,[147] Armstrong,[148] and Sutherland[149] have made similar suggestions based on other types of measurement. If the complex water molecules are dissociated, then the concentration of the solution in respect to the solute is diminished and the molecular weight from the observed osmotic pressure becomes greater. Such a mode of explanation is not easy to test, and it must be pointed out that association of benzoic and acetic acids occurs in nitrobenzene, a substance whose molecules are simple, according to current conceptions.

On the other hand, if the association in water is real and not apparent, it may be of the same type as that which is exhibited by colloidal substances; and this at any rate can be said for the view, namely, that the substances on the whole least soluble in water are the ones most associated, just as colloids do not dissolve to form a true aqueous solution (*cp.* p. 31). But supposing this to be the case, that is, suppose the association in water to be just as real as in any other solvent, then a formidable difficulty of another kind arises. Nernst[150] based his theory of the Partition Law both on examples of normal substances and on the instance of benzoic acid divided between water and benzene. Now, on the assumption that benzoic acid is normal in water and has approximately a double molecule in benzoic acid, Nernst found that the requirements of the law that $\frac{C_w}{\sqrt{C_B}} = k$ (where C_w

is the concentration in water and C_B in benzene), were fulfilled. From the measurements quoted above on the state of benzoic acid in water, it would appear that in this solvent also the molecules are double, and therefore it would be impossible for $\frac{C_w}{\sqrt{C_B}}$ to be constant. In such a case, the simple ratio $\frac{C_w}{C_B}$ ought to be constant. Experiments made in the writer's laboratory at 40° in order to obtain stronger solutions of benzoic acid, showed the constancy of the ratio $\frac{C_w}{\sqrt{C_B}}$. The problem is, therefore, at present at an interesting stage.

The Effect of Dielectric Constant on Electrolytes as Solutes.

Although the recognition of electrolytes as associated substances is but very recent, the effect of the solvent can be set out more satisfactorily and with greater sureness than in the case of weak electrolytes or non-electrolytes.

The chief difficulty in testing the effect of the solvent on the molecular complexity of salts (for these, together with a few acids, are the only electrolytes yet tested), is their sparing solubility. This difficulty can be overcome, however, by using salts derived from organic ammonium, sulphonium and oxonium bases; for such salts have been found in other respects to behave like the salts of the alkali metals, and so far as metallic salts have been tested, the general regularity shown in the influence of the solvent on organic ammonium salts holds also for metallic salts.[151] With this remark, and reference to the Appendix, the examples chosen for illustration in this chapter will be confined to the salts of organic ammonium bases.[152]

The following table sets out for comparison, in a manner like that for non-electrolytes, the degree of complexity of the four salts diethylammonium chloride, tetraethyl ammonium iodide, tetrapropylammonium nitrate and quinoline ethiodide at the same molecular concentration (calculated from the simple formula), namely, 25 milligram molecules per 100 c.c. of the solvent. Instead of quoting the actual molecular weight, the degree of association, or ratio of the observed to the calculated molecular weight is given, and where the number is enclosed in brackets, it

is obtained by extrapolation and consequently subject to possible error.

DEGREE OF ASSOCIATION IN SOLUTION.

CONCENTRATION, 25 MILLIGRAM MOLECULES PER 100 C.C. SOLVENT.

Solvent.	Dielectric Constant.	Et_2NH_2Cl.	Et_4NI.	$Pr_4N.NO_3$.	C_9H_7NEtI.
Formamide	$>84_{20°}$	0·57	0·58	—	—
Water	$66_{100°}$	0·61	0·66	0·66	0·61
Ethylene cyanide	$61·2_{60°}$	—	0·62	—	—
Formic acid	$58·5_{16°}$	0·68	0·68	—	—
Nitrobenzene	$40·0_{6°}$	—	—	(0·95)	—
Nitromethane	$39·4_{20°}$	—	0·68	—	—
Acetonitrile	$30_{81°}$	1·68	0·70	0·62	—
Propionitrile	$22·5_{98°}$	—	0·77	—	—
Methyl alcohol	$21·0_{66°}$	—	0·80	—	—
Ethyl alcohol	$18·0_{78°}$	1·00	0·99	0·89	1·12
Acetone	$17·0_{56°}$	—	—	1·15	—
Sulphur dioxide	$14·0_{20°}$	1·41	0·78	—	—
Ethylurethane	$13·6_{60°}$	1·27	—	1·06	1·33
Phenol	$9·7_{48°}$	1·24	1·23	1·27	—
Pyridine	$9·5_{116°}$	1·83	(? 2)	—	—
Dimethylethylcarbinol	$7·9_{102°}$	1·24	—	—	—
Acetic acid	$6·3_{16°}$	1·63	—	2·12	—
iso-Amyl alcohol	$5·7_{132°}$	1·48	1·87	1·73	2·29
p-Toluidine	$5·4_{44°}$	1·55	1·45	1·51	1·67
Bromoform	$4·3_{7·5°}$	3·03	—	—	—
Chloroform	$4·1_{3_{61·2°}}$	2·53	—	5·0	(? >4)
Diphenylamine	$3·3_{51°}$	1·98	5·0	3·98	—

The results in all cases (and the salts chosen for illustration are but types) indicate that the observed molecular weight is very low in solvents of high dielectric constant, rising steadily with decrease of the dielectric constant until, when the latter becomes small, the molecular weight is very high. This transition would certainly be more regular if the determinations were made under precisely the same conditions of temperature, conditions impossible of attainment. Thus, the tests in acetic acid were carried out at 16° while those in amyl alcohol were made at 132°, a difference of temperature which will certainly account for the break in the order given (*cp.* p. 32). Again, the lower values with *p*-toluidine are most probably due to combination in solution. On the whole, therefore, it can be said that for salts, the apparent molecular weight is controlled mainly by the dielectric constant of the solvent.

Specific influences, due to the nature of the solute and of the solvent, are not absent. Thus, diethylammonium chloride, and *iso*-butylammonium chloride, are both distinctly associated in acetonitrile, of high dielectric constant, whilst the same remark

applies to hydrogen chloride in nitrobenzene.[153] In the case of the solvent, influences which cannot be ascribed to the dielectric constant or to the employment of different temperatures are not absent, as illustrated by a comparison of chloroform and diphenylamine.

In the light of the preceding results, the abnormally low molecular weight values found for salts in water, results on which the theory of electrolytic dissociation was largely based, no longer stand out as abnormal, but fall into line with those obtained in other solvents. Electrolytic dissociation and molecular association in the case of electrolytes appear therefore as parts of a general phenomenon; they are complementary, the precise molecular condition being a matter almost wholly of the dielectric character of the solvent.

The point at which, in the dielectric constant list, molecular association begins to be apparent cannot well be decided because the molecular association depends on the concentration also; but in solutions which are not really concentrated, association is clearly in evidence for a number of salts, such as tetrapropylammonium iodide and quinoline ethiodide[152] in alcohol, and in acetone the indication is still clearer. As the dielectric constant of alcohol is 18·0 at its boiling point, this value may be considered as the one below which molecular association begins to be evident. Nor is this the case with salts alone; for amides and anilides show a tendency, except in quite dilute solution, to association in alcohol and acetone.[144] With salts, except chlorides, in a few cases, a dielectric constant above 18·0 leads to a molecular weight below the normal.

Finally, it may be pointed out that the associated condition of a solvent does not endow it with dissociating power, unless, at the same time, its dielectric constant is high. Thus, water, formic acid, formamide, acetonitrile (except with chlorides) and ethylene cyanide are associated substances which do produce dissociation of salt molecules; but dimethylethylcarbinol, phenol, acetic acid, and *iso*-amyl alcohol are also associated yet permit pronounced association. The first five have high dielectric constants, however, the remainder only low values. For weak electrolytes and non-electrolytes this is likewise true. Discounting association in water, both benzoic acid and acetic are strongly associated in liquid nitrogen peroxide and the former also in ethylene cyanide (see p. 43).

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CHAPTER V.

MOLECULAR COMPLEXITY IN THE LIQUID STATE.

THE determination of the molecular condition of matter in any condition other than the diluted state is attended at present with very considerable difficulties. Avogadro's hypothesis makes determinations in the case of gases and dilute solutions a very simple matter in theory, but for liquids there is at the present time no similar guiding principle. With one or two exceptions, indeed, all the methods available are empirical.

The basis of most methods, therefore, consists in instituting a comparison of the molecular properties of different liquids. As the outcome of such tests, it is found that the molecular property depends very largely on the molecular weight of the substance; that is to say, the property is additive. As such, it is possible to express it in simple mathematical form as an equation involving the molecular weight and a constant. Thus, Trouton's Rule (see p. 52) is the expression of the experimental fact, that the heat required to evaporate a molecular weight in grams of a given liquid is proportional to the absolute temperature of the boiling-point, or

$$M\lambda = k\mathrm{T}.$$

Such generalizations on molecular properties are almost always subject to exceptions, so that it is possible to divide liquids into two classes, those which obey the rule, and those for which k is greater or less than the usual value. The value of M adopted in all expressions such as the above is the molecular weight which the substance has in the state of vapour. Whether M is truly the molecular weight of the liquid will be discussed later, but this much can be said, namely, that for the large body of liquids which obey the given equation, the degree of complexity must be the same, and either, on condensation from the gaseous state, no change of molecular size occurs, or, a change

in complexity in every case the same occurs yielding an aggregated molecule which undergoes no variation in size in the liquid state. Such substances are commonly spoken of as normal.

The most obvious explanation to account for the second or abnormal class, is to suppose that the molecular weight is not truly represented by M, but that it is either greater or smaller, and is represented by xM, where x represents the degree of complexity, which can be determined knowing the other quantities in the equation. This explanation is rendered very probable because it is found that substances associated in solution, are always abnormal in the liquid condition. Hence, it is but a natural conclusion to assume that the real molecular weight is not M but xM, where $x > 1$. Both qualitative and quantitative methods of determining association follow such lines. In the present chapter certain qualitative evidence of association will be given, but it is easy to discern that many of the methods quoted could, without difficulty, be extended also to a quantitative determination.

Evidence of Molecular Association in Liquids.

1. *From Vapour Pressure Data.*—It is a very common occurrence that a substance which is volatile possesses in solution the normal or simple molecular weight, and it is only a step to the deduction that association of a liquid will diminish its vapour pressure. Thus, one finds that sulphuric acid at ordinary temperatures possesses a scarcely measurable vapour tension, a fact which receives ready explanation from its associated state.[154]

The effect of molecular association on the vapour pressure comes out clearest when tested by the expression of van der Waals,[155] $\log p_c - \log p = k \frac{T_c - T}{T}$, by which the vapour pressure of a liquid can be calculated from the critical temperature and pressure, T_c and p_c, and the temperature T for which p is required. The constant k was found by Young[156] to have a mean value of 3·06 for a large number of substances; but for hydroxylic substances the factor k is not constant and always exceeds 3·06, as the following results indicate:—

Water	3·20-3·24	Ethyl alcohol . .	3·58-4·02
Methyl alcohol . .	3·56-3·77	Propyl alcohol . .	3·49-3·77
Acetic acid	3·36-3·49		

The fact that these substances in solution can exist as complex molecules renders an explanation of these abnormal results as due to association an obvious one.

2. *Boiling-point Evidence.*—(*a*) Just as the vapour pressure may be diminished by association, so the boiling-point will be raised. Now the boiling-point, although not strictly an additive property, has been demonstrated to be very largely influenced by the mass of the molecule, so that it is possible to calculate the boiling-point, very approximately, of a given substance, knowing its chemical composition, by adding the values for the elements. In this way the value calculated by van't Hoff for water is − 207° instead of + 100°.[157]

Walden[158] proceeds in a somewhat different manner. Methyl sulphide (B.-pt. 37°) has a boiling-point 60° higher than methyl ether (B.-pt. − 23°), whilst the difference between ethyl sulphide and ethyl ether is 58·4°. Substitution of oxygen by sulphur, therefore, raises the boiling-point, on the average, 59°. Compared with sulphuretted hydrogen (B.-pt. − 61°) water therefore should boil at − 120°. The actual boiling-point, 100°, can readily be accounted for if liquid water is associated.

(*b*) Another way in which the effect on the boiling-point can be indicated is by means of the equation

$$\frac{T'_A}{T'_B} = \frac{T_A}{T_B} + C\,(t' - t)$$

relating the boiling-points under different pressures of two substances A and B, T_A and T_B being the respective boiling-points under the same pressure, T'_A and T'_B the boiling-points under some other common pressure, and t' and t the boiling-points of either of the substances under the given pressures, and c a constant. When A and B are very closely alike in properties, as, for example, chlorobenzene and bromobenzene, c becomes exceedingly small. In any case, the equation for most substances corresponds to a straight line, but for alcohols and aliphatic acids it does not.[159] Again, the deviation may be explained by assuming the associated condition of these hydroxylic substances.

3. *Latent Heat.*—Closely connected with the boiling-point is the latent heat absorbed during the passage from liquid to vapour. Unless there is a difference between the molecular state of the liquid and the vapour, the heat imparted will be employed in

performing external work. A dissociation into a simpler molecular state will call for an increased supply of heat, that is to say, the latent heat of associated substances tends to be high. An explanation, depending on association, has also been suggested for the maxima observed in the latent heat of some liquids, such as with ethyl alcohol, the latent heat of which reaches a maximum at 10° and acetic acid at 120°.[160]

Trouton's Rule enables one to test the molecular state of a substance by a measurement of its latent heat. As previously stated, the mathematical expression of the rule is

$$\frac{Ml}{T} = \text{constant.}$$

Although strictly the equation should apply only to similarly constituted liquids, as it is only for similar substances that corresponding states can be realized,* it is found in practice to hold for a large number of substances. An investigation by Walden [161] has proved the average value of the constant to be 20·7, and that departure from this rule, either by a higher or a lower value, may be taken as evidence of molecular association. Thus, in the following table, are both types of deviation from $k = 20{\cdot}7$.

Substance.	$\frac{Ml}{T}$.	Substance.	$\frac{Ml}{T}$.
Water	25·9	Acetonitrile	17·74
Formic acid	14·8	Propionitrile	19·97
Acetic acid	14·88	Butyronitrile	20·33
Methyl alcohol	24·67	Valeronitrile	19·89
Ethyl alcohol	28·3	Acetone	22·2
Phenol	28·2		

The high numbers appear to be obtained with hydroxylic substances, low values with organic acids and nitriles.

It might be thought that the method should be capable of use in determining the molecular weight, or at any rate that the extent of deviation from the mean value for normal substances should indicate the extent of association, but comparison with methods given in the next two chapters will show that it does not serve such a purpose. Phenol, for example, deviates much more than either water or methyl alcohol although less associated than either. In this connexion what has already been said about the comparison being limited to substances of similar

* For the derivation of the equation thermodynamically see van't Hoff, "Lectures on Theoretical and Physical Chemistry," Part III, p. 57.

constitution must be borne in mind. Nernst[162] has found that the value of $\frac{Ml}{T}$ depends on the boiling-point of the substance, and increases as the boiling-point rises, so that for hydrogen the ratio is only 12·2. Further, he has shown that

$$\frac{Ml}{T} = 9{\cdot}5 \log T - 0{\cdot}007\ T$$

when the substance is normal, but when associated,

$$\frac{Ml}{T} > 9{\cdot}5 \log T - 0{\cdot}007\ T.$$

Thus, for water and ethyl alcohol the ordinary expression gives values 25·9 and 26·9 (quoted by Nernst) respectively, whilst the new equivalent leads more to the normal value, 21·8 for water, and 21·7 for alcohol being the actual figures. The low value for acetic acid, he suggests, occurs because the vapour molecules are also associated, which is not the case with alcohol. When the actual molecular weight, 97, in the state of vapour is employed for M, then $\frac{Ml}{T}$ becomes 22·1. For acetic acid the value of 9·5 log T − 0·007 T which, it will have been noticed, does not contain the molecular weight as a term, amounts to 21·9.

Although Nernst's explanation may apply to acetic acid, it does not appear to apply to the nitriles, for experiments on acetonitrile vapour in the writer's laboratory do not indicate any appreciable association, like acetic acid, and Trouton's Rule must therefore be considered at best as only affording qualitative evidence of association (*cp.* also application of method in chap. VII.).

Traube[163] has applied the Rule to test the molecular state of bismuth, iodine, sulphur, zinc, cadmium, mercury, and bromine, calculating the latent heat from the thermodynamic formula

$$l = T \cdot \frac{dp}{dt}(v_1 - v_2).$$

The normal value of Trouton's Constant was found in all cases except sulphur, where it had the value 30·2. For the metals the monatomic state appeared to be the normal liquid condition.

4. *Evidence from Critical Data.*—

(*a*) *Divergence from the Rectilinear Diameter.*—The now well-known rule of Cailletet and Mathias for the determination of the critical volume of a substance is based on the observation that

the mean values of the densities of the saturated vapour and the liquid with which it is in contact lie on a straight line (the rectilinear diameter) passing through the critical point. Subsequent investigations[159] have proved that the rectilinear diameter has in a number of cases a very slight curvature which can be readily corrected, but not for alcohols and water. Here the curvature is quite distinct. The inference is that the liquid and vapour in contact have different degrees of complexity. Acetic acid, however, gives a diameter nearly straight, as with this substance both the liquid and the vapour are associated.

(*b*) *Irregularities in the Critical Volume.*—The determination of critical volume provides a second test of molecular association; for Young and Thomas[164] discovered that most liquids have a density at the critical temperature of 3·85 times the value calculated on the basis of the gas laws. Once again the alcohols and acetic acid are abnormal, their factors being

Methyl alcohol	4·52
Ethyl alcohol	4·02
Propyl alcohol	4·02
Acetic acid	5·00

(*c*) *Evidence from the Value of the Critical Coefficient.*—Utilizing as a basis the characteristic equation of van der Waals applied at the critical point, namely,

$$\tfrac{3}{8}(1 + a\theta) = \frac{\pi\phi}{(1 + 3\pi\phi^2)\left(1 - \frac{\phi}{3}\right)},$$

together with Maxwell's electro-magnetic theory of light and Clausius' equation connecting the dielectric constant with the ratio of the actual to the apparent volume of the molecules of a substance, Guye[165] obtained a relationship

$$\frac{273 + \theta}{\pi} = \frac{1}{f} \cdot \mathrm{MR},$$

where $(273 + \theta)$ represents the absolute critical temperature (T_c) π the critical pressure (p_c), MR the molecular refraction and f a constant. Now the value of f which a large number of normal substances have is 1·8, but for water, methyl alcohol, and acetic acid it amounts only to about 1·1.

It will be clear that since the equation contains the value of the molecular weight M, it should be possible to determine the molecular complexity of an associated substance. This has been

done. Unfortunately, the method is limited to the critical temperature and therefore also involves practical operations which are not easy to perform.

Other evidence of association is forthcoming from a study of corresponding states.[159] At a given reduced pressure $\frac{p}{p_c}$, where p is the pressure employed and p_c the critical value, the ratios $\frac{T}{T_c}$, $\frac{v_l}{v_c}$ and $\frac{v_v}{v_c}$, where T_c and v_c are the critical temperature and volume, respectively, T the temperature at pressure p, and v_l and v_v the corresponding volumes of liquid and vapour, should be constant for all substances. Although not perfectly true for normal substances, the divergencies in the case of the alcohols and acetic acid are much greater.

5. *Evidence from Viscosity Measurements.*—If the viscosity of a series of substances is tested, it is found to increase in value as the molecular weight rises. A high viscosity, therefore, indicates usually a high molecular weight; so that if the simplest molecular weight of the substance examined is low, the inference to be drawn from a high viscosity is that association of molecules has occurred. In the main this is the argument on which the viscosity test of association rests. Thus, Thorpe and Rodger, from the rather high and irregular viscosities of the alcohols and aliphatic acids, supposed association to occur.

There are several methods, mainly the work of Dunstan and his collaborators, in particular Thole, of demonstrating the existence of association by means of viscosity data. One method * depends on the discovery that the expression $\frac{\eta}{Mv} \times 10^6$, where η is the viscosity coefficient and Mv the molecular volume is a constant quantity for series of like substances. Thus :—

Substance.	$\frac{\eta}{Mv} \times 10^6$.	Substance.	$\frac{\eta}{Mv} \times 10^6$.
Benzene	65	Alkyl chlorides	37·4
Chloroform	67	Alkyl bromides	50·7
Carbon disulphide	60	Alkyl iodides	68·3
Ethers	25·2	Ketones	43·3

All the substances contained in this table are normal. When

* For a fuller account of the effect of association on viscosity, reference should be made to Dunstan and Thole's "The Viscosity of Liquids" in this series.

association occurs, the value of the expression is much higher, as in the following examples :—

Substance.	$\frac{\eta}{Mv} \times 10^6$.	Substance.	$\frac{\eta}{Mv} \times 10^6$.
Water	493	Formamide	181
Methyl alcohol	138	Acetamide	219
Ethyl alcohol	189	Propionamide	162
Acetic acid	195	Urethane	103
Glycerine	106,000		

A variety of other methods, especially in the case of water, have been proposed for the detection of association in liquids, and will be referred to in chapters VII. and VIII.

CHAPTER VI.

SURFACE TENSION METHODS OF DETERMINING MOLECULAR COMPLEXITY IN THE LIQUID STATE.

SURFACE tension methods of investigating the molecular condition of liquids, methods which have received far greater attention than any other, may be divided roughly into two classes according as they are related to the Ramsay and Shield's method and depend on the measurement of surface energy, or as they are based on a study of the specific cohesion, as in the methods of Kistiakowsky, Walden, Dutoit and Moijou.

The method of Ramsay and Shields [166] which has exerted so great an influence on other methods, and was indeed the first by which insight was obtained into the molecular state of liquids, depends on a study of the temperature coefficient of molecular surface energy, as expressed in the equation

$$\gamma (M v)^{\frac{2}{3}} = k (T_c - t - d^\circ) = k (\tau - d)$$

in which γ, M, and v represent the surface tension, molecular weight, and specific volume of the substance at the temperature τ measured from the critical temperature (T_c) downwards, and k is a constant.

The above equation differed from that of Eotvos,[167] whose work underlay that of Ramsay and Shields, in the factor d°, usually 5° or 6°, a correction necessary because the surface tension varies proportionately with the temperature only from some point a little way below the critical. In defining the molecular surface as $(Mv)^{\frac{2}{3}}$, Ramsay and Shields followed Eötvos, assuming that the molecules at the liquid surface are distributed in the same manner as throughout the rest of the liquid. For this assumption, they stated explicitly that there was no direct evidence, but that the results of the method appeared to make the assumption justifiable. It is possible that the abnormal results found later may be due to this assumption not being wholly true. The

value of k,

$k = \dfrac{\gamma(\mathrm{M}v)^{\frac{2}{3}}}{\tau - d} = \dfrac{\Delta \mathrm{E}_o}{\Delta t}$ (a shorter expression sometimes employed) was found for a number of liquids which could reasonably be assumed as normal, to have the mean value of 2·121 over a range of temperature from about −90° up to the critical point.

The equation $\gamma(\mathrm{M}v)^{\frac{2}{3}} = k(\tau - d)$ has an analogy to the gas equation PV = RT, in that in the former the molecular surface energy is expressed as proportional to the temperature measured from the critical point, in the latter the molecular volume energy as proportional to the absolute temperature ; and just as association or dissociation of the molecules of a gas affect V or P and will be reflected in the value of R, so, in like manner for a liquid, a variation in the value of k should indicate similar changes.

Suppose, then, that a liquid is abnormal. If the requisite measurements have been carried out, the value of the factor in the equation will no longer be k but some other value, k_1, if the numerical value of the molecular weight employed is the normal value, M. The equation thus becomes

$$\gamma(\mathrm{M}v)^{\frac{2}{3}} = k_1(\tau - d) \quad . \quad . \quad . \quad (1)$$

By inserting the true value of the molecular weight, the factor will assume its normal value, namely, $k = 2{\cdot}12$. Let this true molecular weight be $x\mathrm{M}$, where x is the degree of complexity. Then

$$\gamma(x\mathrm{M}v)^{\frac{2}{3}} = k(\tau - d) \quad . \quad . \quad . \quad (2)$$

By comparing (1) and (2)

$$x = \left(\frac{k}{k_1}\right)^{\frac{3}{2}} = \left(\frac{2{\cdot}12}{k_1}\right)^{\frac{3}{2}}.$$

The determination of the factor d would make the method rather difficult, but the necessity of evaluating d can be removed by making measurements at two different temperatures, when the following relations hold :—

$\gamma_1(\mathrm{M}v_1)^{\frac{2}{3}} = k(\tau_1 - d)$

$\gamma_2(\mathrm{M}v_2)^{\frac{2}{3}} = k(\tau_2 - d)$, neglecting any molecular change between τ_1 and τ_2, so that M and k remain constant.

By subtraction

$$\frac{\gamma_1(\mathrm{M}v_1)^{\frac{2}{3}} - \gamma_2(\mathrm{M}v_2)^{\frac{2}{3}}}{\tau_1 - \tau_2} = k$$

and $\tau_1 - \tau_2$ is merely a temperature interval independent of any scale. A second method is to write the equation in the differen-

tial form (see p. 61). The practical measurements involved are those of surface tension and density.[168] *

The following table drawn from different sources is representative of different types of substances and will indicate the degree to which liquid substances appear to be associated.

Substance.	Temperature.	*k*.	*x*.
Water	0°-140°	0·87 -1·21	3·81-2·32
Methyl alcohol	16·0°- 78·0°	0·933-0·969	3·43-3·24
Ethyl alcohol	16·0°- 78·0°	1·083-1·172	2·74-2·43
Acetic acid	16·0°-132·0°	0·900-1·074	3·62-2·77
Acetone	16·8°- 78·3°	1·818	1·26
Phosphorus (P_4)	78·3°-132·1°	2·205	0·94
Nitrogen peroxide (N_2O_4)	1·6°- 19·8°	2·110	1·01
Phenol	46·0°-184·0°	1·682-1·899	1·42-1·18
Nitroethane [169]	16·6°- 79·6°	1·647-1·684	1·46-1·41
o-Chlorophenol	12·7°- 73·3°	2·20 -2·00	1·0
p-Chlorophenol	51·6°- 99·8°	1·86 -2·03	1·22-1·08
o-Cresol	39·6°- 99·7°	1·97 -2·04	1·12-1·06
m-Cresol	19·1°- 99·9°	1·63 -1·73	1·48-1·33
p-Cresol [170]	45·5°- 99·8°	1·54 -1·82	1·62-1·26
n-Propylamine	10°- 45°	1·84	1·24
iso-Amylamine	20°- 60°	1·955-2·015	1·13-1·08
Dimethylnitrosoamine	20°- 75°	1·745-1·945	1·34-1·14
Formamide	20°- 75°	0·63 -0·95	6·18-3·34
Acetamide	85°-120°	1·16 -1·29	2·47-2·11
Lactamide	80°-120°	1·05 -1·14	2·87-2·54
Benzamide	130°-170°	1·095-1·43	2·70-1·81
Formanilide	60°-105°	1·485-1·725	1·69-1·36
Ethyl urethane [171]	60°-105°	1·495-1·57	1·69-1·57
Acetonitrile [172]	20°- 60°	1·47 -1·56	1·73-1·58
Lactonitrile [171]	20°- 60°	1·255-1·325	2·21-2·03
Propionitrile [173]	20°- 60°	1·63 -1·66	1·48-1·44
Sodium nitrate	330°-400°	0·445	10·68
Potassium nitrate [174]	341°-407°	0·503	8·73
Silver chloride	446°-580°	0·959	3·29
Lead chloride [175]	480°-600°	0·903	3·60

Criticism of the Ramsay and Shields' Method.

Subsequent work has considerably reduced the value of the Ramsay and Shields' method. The criticisms which have been levelled at it as a means of actually measuring the degree of association are (1) that the equation requires modification, (2) that the value of the factor *k*, 2·12, is not always valid, (3) a much more sweeping criticism, that surface tension methods of measuring the molecular complexity do not afford a true indication of the molecular state of the liquid as a whole.

* For apparatus and details of measurement see Ramsay and Shields, Hewitt and Winmill, Turner and Merry, Walden, Dutoit and Moijou.[168]

The need of a more accurate method of determining the value of x was recognized by Ramsay himself, and before the appearance of other criticism, he revised the original expression and employed another deduced by Rose-Innes,[160] namely,

$$\gamma\,(\mathrm{M}v)^{\frac{2}{3}} = \frac{k_1\,(\tau - d)}{1 + \mu\tau},$$

where μ and k_1 are new constants to be derived for the substance. This formula was found to represent the variation of the molecular surface energy of water, the alcohols and acetic acid, over a range of temperature from 30° below the critical point down to low temperatures.*

Now, as previously stated, the original equation for associated liquids becomes

$$\gamma\,(x\mathrm{M}v)^{\frac{2}{3}} = k\,(\tau - d), \text{ where } k = 2{\cdot}121.$$

Dividing this by the Rose-Innes equation,

$$x = \left[\frac{2{\cdot}121}{k_1}\,(1 + \mu\tau)\right]^{3/2}.$$

When applied by Ramsay to the earlier experimental data, the following numbers were obtained:—

Substance.	Temperature.	k_1.	μ.	x.
Water	0°-140°	2·631	0·00218	1·707-1·289
Methyl alcohol	−89·8°-220°	1·489	0·00104	2·65 -1·75
Ethyl alcohol	−89·8°-230°	2·170	0·00193	2·03 -1·00
Acetic acid	20·0°-280°	1·910	0·00163	2·13 -1·30

A noticeable reduction in the value of the degree of association is brought about by the new formula. Indeed, Tyrer argues that the results now obtained are too low, the original equation probably giving more correct results, because the value of the critical temperature required in the new formula depends on the degree of complexity and will accordingly be variable (*see more fully*, Batschinski, p. 65). The real source of error in the original equation, apart from the principle, lies, according to Tyrer,[177] in neglecting the variation of molecular complexity with temperature over the range for which k is found. For the equation

* A still more accurate expression [160] is

$$\gamma\,(\mathrm{M}v)^{\frac{2}{3}} = \frac{k_1\tau - k_1 d\,(1 - 10^{-\lambda\tau})}{1 + \mu\tau},$$

where λ is a new constant. A somewhat similar formula is that of van der Waals,[176] namely,

$$x^{\frac{2}{3}} = \frac{k\,(\tau_1 - \tau) + \gamma\,(\mathrm{M}v)^{\frac{2}{3}}}{\gamma\,(\mathrm{M}v)^{\frac{2}{3}}}.$$

$\gamma(x\mathrm{M}v)^{\frac{2}{3}} = k(\mathrm{T}_c - t - d)$, written in the differential form becomes

$$x^{\frac{2}{3}}\frac{d}{dt}\gamma(\mathrm{M}v)^{\frac{2}{3}} + \gamma(\mathrm{M}v)^{\frac{2}{3}}\frac{d}{dt}x^{\frac{2}{3}} = k\frac{d\mathrm{T}_c}{dt} + k.$$

The second term was taken into account in the revised formulæ used by Ramsay, but the third was neglected as being too small. In practice it cannot always be neglected.

The second cause for criticism arises from the fact that the value of k, originally thought to lie very closely in the neighbourhood of 2·12, may, even for non-associated substances, vary widely from this value. Even Ramsay and Aston[178] noticed that several esters had values of k between 2·2 and 2·3, but did not study the ester series sufficiently to discover the abnormalities which subsequent investigators brought to light. Thus, the higher esters of malic acid,[179] amines, which show in a very clear way the effect of substitution and increase in the molecular weight on the value of k, phenylurethane and the alkylated anilides,[171] tristearine and tripalmitine,[180] and many other substances,[181] have values of k much higher than 2·12, as the following table shows :—

Substance.	Temperature.	k.
Pelargonylethylmalate	12·3°-105·0°	3·68 -3·38
Caprinylethylmalate	16·3°-106·6°	3·59 -3·46
Amyl stearate	54·6°-150·0°	3·34 -3·33
Benzylamine	20°- 75°	2·08 -2·225
Dibenzylamine	20°- 75°	2·805-3·00
Tribenzylamine	95°-135°	3·41 -3·58
Amylamine	20°- 60°	1·955-2·015
Triamylamine	20°- 75°	3·105-3·185
Tristearine	57·7°-134·7°	6·21 -5·35
Tripalmitine	55·7°-125·1°	4·92 -4·96

If the mode of interpretation set out by Ramsay and Shields is to be strictly followed, then the above substances must be regarded as undergoing dissociation in the liquid state, to such an extent that tribenzylamine is split into two parts (x = 0·49 – 0·47) and tripalmitine into four or five (x = 0·203 – 0·240). But there are many cogent reasons why this is improbable; for molecular weight determinations in several solvents give no indication of the extensive association suggested from the determination of k[171, 180]. Moreover, the coefficients of surface energy of tristearine and tripalmitine in benzene solution have nearly the normal value, Trouton's Constant for the esters tabulated has

the normal value,[182] and several other methods of determining the molecular complexity of liquids one and all afford evidence against the hypothesis of dissociation. Homfray and Guye,[179] however, favoured the hypothesis of dissociation and, more recently, Guye[183] has put forward the view that the esters are dissociated into hydrocarbon and acid by reason of the powerful forces acting on the surface film of a liquid, in which part alone, he considers, the dissociation takes place. On this ground, he regards the Ramsay and Shields method as unsatisfactory, since the molecular state of the liquid at the surface and in the interior will be different.

The whole subject of the variation of the temperature coefficient, k, has been systematically attacked by Walden and Swinne, who find that its value is really a function of molecular constitution. Thus, whilst certain groups tend to produce association, the values of $\frac{\Delta E}{\Delta t} = k$, as also the temperature coefficient of molecular cohesion, $\frac{\Delta\, Ma^2}{\Delta t}$ (*vide*, p. 71) are affected by substitution. An increase in the value of the coefficient accompanies, for example, substitution of CH_3 by C_6H_5, of O by S, N by P or Sb, Cl by Br, and Br by I in a measure approximately quantitative, whilst a steady rise always occurs in a homologous series. As in every case, these changes are accompanied by an increase in mass, it is obvious that, despite minor constitutive influences, the temperature coefficients, both of molecular surface energy and molecular cohesion are additive properties. Two striking facts give proof of this. The first is that tripalmitine and tristearine, the substances of highest molecular weight so far investigated, have also the greatest temperature coefficients; the second, and still more conclusive, that the additive character can be expressed by the empirical formulæ

$$\frac{\Delta E}{\Delta t} = -\,[1{\cdot}90 + 0{\cdot}011\ (\Sigma\sqrt{A})]$$

$$\frac{\Delta Ma^2}{\Delta t} = -\,[0{\cdot}00027\ (\Sigma\sqrt{A}) + 0{\cdot}0103] \text{ where } t = 100°,$$

and $\Sigma\sqrt{A}$ represents the sum of the square roots of the atomic weights of the constituent elements, and by means of these formulæ the values of the coefficients can be calculated for many substances of widely different character and molecular weight.

The great differences possible in the molecular weights of

different liquids may be attended by another consequence, namely, a wide variation of critical temperature. Now in order to compare accurately the values of the molecular surface energy, as of any other physical property, the comparison ought strictly to be carried out at corresponding temperatures, a condition which in practice it is most difficult to attain. The manner in which k varies, decreasing with rise of temperature as with tristearine and tripalmitine suggested the possibility that at the critical temperature, at which all substances are in corresponding conditions, normal values might be obtained. In order to test this possibility, Walden and Swinne calculated the values of the critical temperatures by the aid of the Batschinski formula (p. 66) and on extrapolating the value of k to this temperature, found it to have the value 2·11 for tripalmitine and 2·06 for tristearine. While these two substances lend most favourable support to the suggestion, a number of others are known for which the coefficients rise with the temperature, so that the normal value at the critical point could not, with good reason, be predicted.

As to the dissociation hypothesis of Guye, Walden and Swinne brought forward several arguments which were not in harmony with it. But the most obvious arguments, in the writer's opinion, lie in the additive character of the coefficients, and in the widely differing classes of substances showing these high values, substances the mode of dissociation of which it would be difficult to surmise.

To sum up the evidence of this section, Ramsay and Shields' method leads in some cases to low values of k, values which can with confidence be explained as due to molecular association ; in some other cases, now known to exceed in number the original normal examples of Ramsay and Shields, high values are obtained which cannot be explained by the reverse process of dissociation. Against such a supposition, the results of other methods of determining the molecular complexity of liquids, for example, Trouton's Rule, already dealt with, Walden's, Kistiakowsky's and that of Dutoit and Moijou all yet to be discussed, are in agreement. As the deduction of the degree of association by Ramsay and Shields' method involves the use of a factor k which varies widely even for normal substances, it is obvious that the true molecular complexity cannot be calculated. There is the possibility, however, especially in view of the additive char-

acter of k of limiting the method to substances having molecular weights within a certain range, dividing substances, that is to say, into groups having molecular weights within a certain range and finding the value of k for such a restricted group, that quantitative results expressing at least the relative order of complexity might be obtained.

Three other methods, related to Ramsay and Shields' method, will now be described. Two of them seek to correct the original method, the third, however, deviates considerably.

Morgan's Method.

This method [184] is really only qualitative, enabling one merely to discover the existence of association ; but it is more appropriately described here than in the preceding chapter. The author of the method believes that some of the difficulties arising from the use of the Ramsay and Shields' method are due to the mode of measuring the surface tension.

In the course of experiments on the weight of a falling drop formed at and falling from the end of a tube under no force save that of gravity, Tate [185] found that the weight of the drop was proportional to the weight which would be raised in the same tube by the force of capillarity ; that is to say, the weight of the falling drop is proportional to the surface tension.*

It is this fact, tested by Morgan and his co-workers for liquids other than water, which forms the basis of the method.

Supposing w to be the weight of a drop formed under the conditions stated, then w is proportional to γ, the surface tension, and the Ramsay and Shields' equation may be written

$$w\left(\frac{M}{d}\right)^{\frac{2}{3}} = K_B\,(t_c - t - a)$$

where d is the density of the liquid, a corresponds to $d°$ in the original equation, t_c and t are the critical temperature of the substance and the temperature of experiment, respectively, and K_B is a constant for the particular glass tip at which the drop is formed. To standardize the apparatus and determine K_B, benzene, of critical temperature 288·5°, is employed, and the value of w determined for drops falling from capillary tubes bevelled at the end at an angle of 45°, so as to give tips of from 4·5 mm. to 5·5 mm. diameter.

* Lohnstein [186] however, argues that this relation is, in general, not true.

If desired, the surface tension of the liquid can be deduced from the formula $\frac{wk}{K_B}$, where k is the Ramsay and Shields' constant and K_B that in Morgan's formula. In this way, it is maintained, more consistent measurements of the surface tension can be made than by the method of capillarity or any other method.

It is unnecessary, however, to find the value of γ in order to determine whether a liquid is or is not associated. The test applied is to calculate the value of t_c in the above equation. Should the value be independent of the temperature of measurement, the liquid is regarded as non-associated, and in this case, from the experimentally determined value of t_c, M, the molecular weight, can in turn be measured.

Supposing, however, the value of t_c varies with the temperature throughout the series of measurements, then the substance is regarded as associated. By this test, the alcohols and aliphatic acids, formamide, and several ketones have been shown to have higher molecular weights in the liquid than in the gaseous state. No attempt has been made, however, to determine the actual degree of complexity, or to attack the real difficulties arising from the surface tension method.

Batschinski's Method.

While the preceding method lays stress on the actual operation by which surface tension is to be measured, Batschinski [187] accepts existing experimental data but modifies the original equation. In doing so he introduces an interesting idea that the associated and non-associated forms of any one substance must be treated, from the physical point of view, as distinct individual substances. The three constants R, a and b of van der Waals' equation, which are characteristic of the individual substance, must be different for the single and complex molecules. Whilst this is true of R and a, b is held to be less dependent on association and may, indeed, be considered as approximately independent [187a]. Therefore, of the critical constants, temperature, pressure and volume, viz.

$$T_c = \frac{8a}{27\,Rb},\ p_c = \frac{a}{27b^2} \text{ and } v_c = \frac{1}{3b},$$

only v_c will be the same for the associated and simple molecules, whereas T_c and p_c will be functions of the condition of the substance. A complex molecule should therefore have a differ-

ent critical temperature and pressure from the single molecular form, provided its degree of complexity could be retained unchanged over the temperature range up to the critical point; but as, in general, the degree of complexity varies with the temperature, so also will the critical, or meta-critical values (T_{mc}, P_{mc}) as Batschinski calls them, alter. If the dissociation of the molecule is complete, only then does the meta-critical become identical with the critical temperature.

Now in the Ramsay and Shields' formula for associated substances,

$$\gamma (x\,Mv)^{2/3} = k\,(T_c - t - d) = k\,(\tau - d),$$

the value of T_c must be substituted by T_{mc}.

To deduce the value of T_{mc}, the variation of some property must be studied at those temperatures for which the surface tension is also measured, or calculated from existing data at other temperatures by known formulæ. The property made use of is the viscosity, in connexion with which Batschinski [188] had previously deduced the relationships

$$\eta T^3 = \text{constant, and}$$

$$\frac{T_c d_c^{\frac{1}{3}}}{(\eta T^3)^{\frac{2}{7}}} = \text{constant,}$$

where d_c and T_c are the critical density and temperature, respectively, η the viscosity and T the absolute temperature of its measurement.

The mean of ten closely agreeing values of this constant, using non-associated substances, hydrocarbons, esters and ether, was found to be 16·31. For associated substances, however, T_c must be substituted by T_{mc}, when it is assumed that

$$\frac{T_{mc} d_c^{\frac{1}{3}}}{(\eta T^3)^{\frac{2}{7}}} = 16{\cdot}31$$

and in turn, that the meta-critical temperature can be calculated by using the value of the constant given. If d_c is unknown, then an alternative, but somewhat less accurate, expression is used,

$$\frac{T_{mc} d_0^{\frac{1}{3}}}{(\eta T^3)^{\frac{2}{7}}} = \text{constant} = 19{\cdot}4,$$

where d_0 is the density at 0°.

Substituting T_c by T_{mc} in the equation of Ramsay and Shields, the values of x may be found, and Batschinski obtained results from which the following is a selection :—

Substance.	Temperature.	$T_{mc.}$	x.
Water	0°-100°	752·3°-581·4°	2·82-1·10
Methyl alcohol	20°	590·1°	3·43
Ethyl alcohol	20°-60°	719·9°-657·6°	4·43-3·65
n-Propyl alcohol	16·4°-78·3°	878·1°-707·4°	5·03-3·15
n-Butyl alcohol	17·4°-77·9°	959·4°-706·7°	4·79-3·03
Formic acid	16·8°-79·4°	783·1°-690·6°	3·80-2·68
Acetic acid	20·0°-100·0°	700·0°-650·6°	3·47-2·74
Propionic acid	16·6°-132·5°	698·9°-656·6°	2·48-2·26

The results of this method are on the whole to enhance the values of the degree of complexity. At the same time it will be noticed that the most associated member of the alcohol series is not methyl alcohol, as usually found, but that association increases with molecular weight up to propyl alcohol.

Bennett and Mitchell's Method.

The total surface energy, λ, of a liquid, given by thermodynamics as

$$\lambda = \gamma - T\frac{d\gamma}{dT},$$

where γ is the surface tension, has been shown by Whitaker [189] to be of more importance for the study of the physical properties of a liquid than the surface tension.

This same quantity, λ, has been connected with the equation of Ramsay and Shields by the following expression due to Kleemann [190]

$$\left(\gamma - t\frac{d\gamma}{dt}\right)(Mv)^{2/3} = 2{\cdot}12\,(T_c - 6).$$

Bennett and Mitchell's method [191] is based on this result. In the first place, the temperature variation of the quantity $\left(\gamma - t\frac{d\gamma}{dt}\right)(Mv)^{2/3}$ which is the *total molecular surface energy*, is only expressed approximately when the numerical constant is 2·12, and Bennett and Mitchell found a more precise relationship

$$\left(\gamma - t\frac{d\gamma}{dt}\right)(Mv)^{\frac{2}{3}} = 2{\cdot}38\,(T_c - 6).$$

Here, then, is an expression very similar in form to the equation of Ramsay and Shields, the difference being that the total surface energy is the fundamental property instead of the surface tension, and the introduction of this quantity slightly alters the constant of the equation.

The total molecular surface energy is written as K, and was

proved to remain constant over a wide range of temperature for each non-associated liquid examined. Moreover, it was found to be additive in character in such a way that values could be assigned to the atoms as indicating their contribution to the total molecular surface energy; so that when K had been determined for a number of normal compounds, atomic surface energies could be determined like atomic volumes or refractions are deduced.

ATOMIC (OR GROUP) SURFACE ENERGIES.

CH_2	83	C_6H_5	990	NOH	820
H	310	CN	870	NO_2	700
C	− 537	CNS	945	Double bond	654
O (in ether)	160	NCS	465	Ring closing:—	
O (ketonic)	780	Cl	600	(1) Hexamethylene	740
N (in NH_2)	0	Br	805	(2) Pentamethylene	717
		I	820	(3) Trimethylene	671

From these values, K can be calculated with fair accuracy for a large number of compounds, only the esters of acylmalic acid and of polybasic acids deviating to any considerable extent, and, save for the esters mentioned, the substances which give an abnormally high value of Ramsay and Shields' constant are normal when subjected to this new test.

From these regularities associated substances are excluded and marked deviation may be employed as a test of association. The actual degree of complexity of associated substances is determined by a study of K, which, although found to be less than the normal value calculated from the atoms, rises regularly with the temperature. Assuming this rise to be due to a continuous breaking down of complex molecules, a constant value may be expected to be arrived at eventually when the substance is no longer associated. This limiting value of K, written as K′, should, when extrapolated from the data at lower temperatures, equal the number calculated for the substance from the atomic values. The importance of being able to calculate K is therefore obvious. For a non-associated substance, there are thus two equations,

$$\left(\gamma_t - t\frac{d\gamma}{dt}\right)(\mathrm{M}v)^{\frac{2}{3}} = \mathrm{K}'_t \quad . \quad . \quad . \quad (1)$$

and

$$\left(\gamma_t - t\frac{d\gamma}{dt}\right)(x\mathrm{M}v)^{\frac{2}{3}} = \mathrm{K}_t \quad . \quad . \quad . \quad (2)$$

much the same as the equations based on Ramsay and Shields' method. When $x = 1$, then K′ has risen until equal to K. From (1) and (2)

$$x_t = \left(\frac{K}{K'}\right)^{\frac{3}{2}},$$

where K′ is the observed value and K the normal, being the sum of the atomic values.

In this way, values of x, calculated from the existing data of other workers, were assigned to the following substances selected as typical examples.

Substance.	T (abs.).	K′ (obs.).	K (calcd.).	x.
n-Propylamine	283°-318°	1044-1098	1179	1·20-1·11
Formamide	293°-348°	952-1058	1173	1·37-1·17
Acetamide	363°-385·5°	1125-1180	1256	1·18-1·10
Acetanilide	398°-425·5°	1830-1850	1936	1·09-1·07
Ethyl urethane	340·5°-370·5°	1240-1280	1416	1·33-1·27

Aliphatic acids and hydroxyl-containing compounds are likewise found to be associated, but owing to the difficulty of deciding on the atomic surface energy to be assigned to hydroxylic oxygen, no values of x were calculated.

Although this method may be admitted as marking a real advance, it raises a number of questions by reason of the difference between its results and those of other methods. Thus, the nitriles appear to be non-associated, the calculated values of K agreeing with the observed, although other methods make them out to be associated. The values of x are also much lower. What is of still greater interest and importance is that the values of x are so much lower than and different in order from the degree of complexity in solution. This question will again be raised in the next chapter.

Methods based on the Specific Cohesion.

Instead of making the surface tension of the liquid the basis of study, the relationship between the surface tension and the density, called the specific cohesion, namely,

$$a^2 = \frac{2\gamma}{d},$$

may be used, a^2 standing to represent the *specific cohesion.*

Several workers on the molecular state of liquids have expressed their measurements in this unit and, curiously enough,

three of them have independently deduced identical rules for the determination of molecular weight involving the specific cohesion.

The specific cohesion which exists in the surface layer of a liquid may be supposed to have a relationship to the amount of heat absorbed during evaporation, and it may be argued that the greater the cohesion the greater must be the amount of heat imported to cause molecules to break through the surface layer and pass into the vapour space. Both Walden [192] and Dutoit and Moijou [193] came independently to the conclusion that the latent heat and specific cohesion would probably be proportional to one another and experiment confirmed this reasoning, as indicated by the following selected results :—

Walden.		Dutoit and Moijou.	
Substance.	$\frac{l}{a^2}$.	Substance.	$\frac{l}{a^2}$.
Stannic chloride	17·35	Pyridine	18·8
Silicon tetrachloride	17·03	Benzene	18·4
Methyl iodide	18·13	Anisole	18·1
Ethyl iodide	17·90	Hexane	18·8
Chloral	17·91	Dimethylaniline	18·1
Carbon disulphide	17·89		

The results are closely the same, being closer still when the mean values are taken of the whole of the substances investigated. By Walden the mean value found was 17·9.

All the above substances are normal; for others, known or suspected of association, such values as the following were obtained (Walden) :—

Substance.	$\frac{l}{a^2}$.	Substance.	$\frac{l}{a^2}$.
Water	44·1	Formic acid	22·8
Methyl alcohol	51·31	Acetic acid	25·08
Ethyl alcohol	45·27	Acetonitrile	29·17
Ethylene glycol	30·86	Propionitrile	25·75
Phenol	27·51	Butyronitrile	23·35
Acetone	24·15	Amylnitrile	18·96

In all cases, unlike Trouton's Constant (p. 52), the values considerably exceed the normal, and the ratio therefore becomes a good test of association. But neither the extent nor the order of association is capable of being satisfactorily determined and the method might have been included in the previous chapter on qualitative tests but for the fact that it has been converted into one for calculating the actual molecular weight. The process adopted by Walden is to combine the above expression with Trouton's Rule. Thus,

$$l = \text{constant} \times a^2 = 17{\cdot}9a^2$$

$$\text{and } \frac{Ml}{T} = \text{constant} = 20{\cdot}7 \text{ (p. 52).}$$

Substituting for l,

$$\frac{M\ 17{\cdot}9\ a^2}{T} = 20{\cdot}7$$

$$\text{or } \frac{Ma^2}{T} = 1{\cdot}162.$$

The quantity Ma^2 is termed the *molecular cohesion*, and the numerical value of the constant 1·162 was confirmed by tests with a large number of non-associated substances.

Precisely the same expression had already been arrived at by Kistiakowsky three years earlier, and although it was then deduced empirically, this same worker has recently placed it upon a theoretical basis.[194] Dutoit and Moijou also based their method on the relationship discovered by Kistiakowsky.

The practical measurement required in this method is that of surface tension and density at the boiling-point T, and if these are known, the molecular weight may be calculated. In the preceding chapter reference has already been made to the fact that the mode of variation of the temperature co-efficient of molecular cohesion, $\frac{\Delta\ Ma^2}{\Delta t}$, with molecular weight, is very similar to that of Ramsay and Shields' constant. But although the high values of the co-efficient of molecular surface energy make the Ramsay and Shields' method inapplicable to substances of high molecular weight, this disadvantage does not attend the Walden-Kistiakowsky method, as will be seen from the following table in which the molecular weights derived by the aid of the formula are compared with the sum of the atomic weights.

Substance.	M.W.	T.	$a^2 \times 10^2$.	M.W. (obs.).
Ethylenedichloride	99	356·3°	4·20	98·4
Benzyl chloride	126·5	451°	4·20	124·6
Nickel carbonyl	171	316°	1·88	195
Chlorobenzene	112·5	405°	4·13	113·8
Diphenylamine	169	575°	3·72	179
Diphenyl	182	557°	3·49	185
Conylene ($CH_3 . C_7H_{11}$)	110	404°	4·062	115
Rutylidene ($C_4H_9 . C_7H_{11}$)	152	478°	3·509	159
Acetylene tetrabromide	168	420°	2·991	160
Hexaethylbenzene	246	571°	2·90	236
Diethylsebacate	258	580°	2·717	256

Nearly all the above substances have abnormally high values of the Ramsay and Shields' constant.

The application to associated substances may now be illustrated by the following table in which x, the degree of association, is $\frac{\text{M.W. (obs.)}}{\text{M.W. (calcd.)}}$.

Substance.	x.	Substance.	x.
Water	1·98	Formic acid	1·78
Methyl alcohol	2·40	Acetic acid	1·95
Ethyl alcohol	1·80	Acetonitrile	1·70
Ethylene glycol	1·40	Propionitrile	1·50
Phenol	1·13	Acetone	1·27

One point in favour of the method is that comparison of different substances is made at the boiling-point, an approximately corresponding temperature. Yet a knowledge is desirable of the molecular complexity at other temperatures. Both Walden and Dutoit and Moijou have attempted to extend the formula, therefore. Walden achieved his object by considering the variation of specific cohesion with temperature, the relation being linear and represented by $a^2_t = a^2_o (1 - K_1 t)$ where K_1 is the temperature co-efficient of specific cohesion. For some lower temperature t, the formula therefore became :—

$$M = \frac{1{\cdot}16\ T_\sigma (1 - K_1 t)}{a^2_t (1 - K_1 t_\sigma)},$$

where T_σ is the absolute boiling-point, t_σ that on the centigrade scale (since the formula for the variation of specific cohesion is based on a^2 at $o°$), and a^{2t} the specific cohesion at the desired temperature t.

The formula of Dutoit and Moijou is empirical, namely,

$$M = \frac{0{\cdot}6\ T (4{\cdot}8 - \log p)}{a^2},$$

and investigation at different temperatures is carried out by varying the pressure under which the liquid boils. For a large number of liquids known to be non-associated, the formula yields excellent results over a wide range of temperatures, and pressures from 1 – 1500 mm., the greatest deviation with benzene, chlorobenzene, ethylene dibromide, dimethylaniline, carbon tetrachloride and quinoline not exceeding 3 per cent.

Still another plan adopted by Walden [195] to extend the Kistiakowsky-Walden rule, is based on the idea that the melting-point may possibly, like the boiling-point, be a corresponding

temperature. If this is so, the method would afford information of the molecular state of substances, such as salts and metals, the high boiling-points of which prevent the application of the original formula. The question whether the melting-point may be regarded as a corresponding temperature was tested by experiment, the result being very favourable to such a view. In the revised formula,

$$\frac{M a^2_\phi}{T_\phi} = \text{constant},$$

T_ϕ and a^2_ϕ being the absolute melting-point temperature and a^2_ϕ the corresponding specific cohesion, the mean value of the constant was determined as 3·65. By means of the new formula the following values of x, the degree of association at the melting-point, were obtained.

Substance.	x.	Substance.	x.
Water	3·58	Urethane	2·16
Formic acid	3·4	Sulphuric acid	1·73
Acetic acid	3·3	Benzene	1·85
Ethylene glycol	1·74	Naphthalene	1·46
Phenol	1·68		

Unlike other methods, this one makes bromine, benzene, and naphthalene appear associated, so that its value, other than as a test of association, is very doubtful.

CHAPTER VII.

MOLECULAR COMPLEXITY IN THE LIQUID STATE.

Some Other Methods and a Review.

Longinescu's Method.[196]

THIS is a method depending on the application of an empirical relationship found to exist between the absolute boiling-point, the density and the number of atoms present in the compound.

For any pair of normal liquids of boiling-points T and T′, respectively, on the absolute scale, densities d and d' at 0°, and containing n and n' atoms per molecule,

$$\frac{T}{T} = \frac{d}{d'}\sqrt{\frac{n}{n'}}, \text{ or } \frac{T}{d\sqrt{n}} = \frac{T'}{d'\sqrt{n'}} = \text{constant},$$

and from the examination of a large number of substances, all normal, the value of the constant was deduced as 100. Conversely, if T and d are known, the number of atoms can be deduced from the formula $n = \left(\frac{T}{100\ d}\right)^2$ and the complexity of the substance therefore deduced.

The two following tables indicate the first the extent of agreement between the calculated (n) and the theoretical number of atoms (n_o) for normal liquids; the second, the number of atoms present in some associated substances.

I. NORMAL LIQUIDS.

Substance.	n_o.	n (calcd.).	Substance.	n_o.	n.
Acetyl chloride	7	8	Ethyl propionate	17	16
Chlorobenzene	12	12	Phosphorus oxychloride	5	5
Ethylene dichloride	6	6	Carbon disulphide	3	6
Silicon tetrachloride	5	5	Sulphur dioxide	3	3
Ethyl cinnamate	25	26	Triphenylamine	32	31
			Octyl ether	51	49

II. ASSOCIATED SUBSTANCES.

Substance.	n_o.	n.	Substance.	n_o.	n.
Formic acid	5	9	Water	3	14
Acetic acid	8	14	Hydrogen fluoride	2	9
Methyl alcohol	6	19	Hydrogen cyanide	3	18
Ethyl alcohol	9	19	Ammonia	4	14
Propyl alcohol	12	20	Phosphorus	4	9
Glycol	10	17	Sulphur	8	12
Propylamine	13	20	Sodium	1	108
Phenol	13	18	Potassium	1	132
Acetanilide	6	19			

The method has been applied by its author to a large number of substances, and where comparison is possible, there is very fair agreement with the results obtained by other methods. Extraordinary results are obtained in some cases, notably with sodium and potassium, but this much is to be said, that some of the very high results are obtained for inorganic substances whose boiling points in many cases require revision.

Latent Heat Methods.

Of these methods there are quite a number, but of all of them the best that can be said is that they serve to detect association only, although they have been applied actually to quantitative determination. One such method is that of Walden,[195] depending on the application of Trouton's Rule to substances at the melting-point. Previous experiment had indicated that the melting-point might be regarded as marking approximately a corresponding temperature for different substances and the molecular cohesion method was then extended to this temperature. The success of the latter method suggested that Trouton's Rule might likewise be found applicable at the melting-point, and experiments with thirty-four normal substances indicated that

$$\frac{Ml_\phi}{T_\phi} = \text{constant} = 13{\cdot}5,$$

l_ϕ and T_ϕ being the latent heat of fusion and absolute melting-point, respectively. The greatest deviation observed was about 10 per cent.

In turn, the molecular weight could be calculated when the value of this constant had been fixed. When applied to known associated substances and to salts, the following results ensued:

Substance.	x.	Substance.	x.
Water	2·57	Silver chloride	2·2
Formamide	1·62	Potassium nitrate	1·7
Ethylene cyanide	4·70	Lead chloride	1·8
Formic acid	1·44	Lead bromide	2·3
Sulphuric acid	1·71	Aluminium bromide	1·8

Probably objections may be urged against this method as against Trouton's Rule in its ordinary form. The occurrence of high and low abnormal values for associated substances tested at the boiling-point does not appear to be experienced at the melting-point. Fair agreement with the results of the molecular

cohesion method is found, but not with those obtained by Ramsay and Shields' method. Thus, by the latter method, Bottomley[174] found the value of x for potassium nitrate as high as 10, and high values were likewise found by Lorenz and Kaufler.[175]

Quite a number[197] of relationships resembling Trouton's Rule have been deduced and applied to the study of molecular complexity, but none of them serves to do more than indicate cases where association probably occurs.

Bingham's Fluidity Method.[198]

This method depends on a comparison of the observed and calculated values of the absolute temperatures at which a given compound has a fixed fluidity (reciprocal of viscosity). If the temperature variation of fluidity is known, it is possible to calculate the temperature at which the fluidity has a fixed value, either 200 or 300 being the comparison value used. The calculation of the corresponding absolute temperature is carried out by assigning temperature values to the elements or groups of elements, and from the table so constructed, adding up the atomic or group values for the compound required. Thus, in a homologous series, it is possible to calculate the temperature at which the fluidity of each member is 300, and therefore also the difference of temperature for successive members, i.e. the difference for CH_2. It is then possible, as in atomic refractions or volumes, to assign values to the elements, to a double bond, a benzene ring and so on. Such values, for a fluidity of 300, are the following :—

Carbon	−110·2	*iso*-Union	−8·2
Hydrogen	67·8	Double bond	131·3
Oxygen	27·1	Benzene ring	164·2

By the addition of these constants, the absolute temperature at which the fluidity of any particular compound reaches 300, is readily obtained. Should the temperature so calculated agree with that observed, the substance is looked on as non-associated; but should the calculated temperature be lower than the experimental, the ratio of the latter to the former is regarded as the measure of the degree of association. The following association factors (x) have been so obtained.

TEMPERATURE (abs.) OF FLUIDITY 300.

Substance.	Calculated.	Observed.	x
Water	162·7	358·5	2·20
Methyl alcohol	188·1	336·9	1·79
Ethyl alcohol	213·5	371·5	1·74
Acetic acid	236·3	407·9	1·73
Methyl formate	236·3	297·5	1·26
Acetic anhydride	309·9	388·1	1·25
Acetone	207·5	289·5	1·23

Traube's Volume Methods.

According to Traube's measurements, a non-associated liquid, when dissolved in water to form a dilute solution, exerts an attractive influence on the water causing a contraction amounting always to 12·2 c.c. for every gram molecule dissolved. For substances which Ramsay and Shields' method indicates to be associated, the contraction brought about is always less than 12·2. On the assumption that the diminution of the contraction is proportional to the degree of association of the substance, it is possible to find the degree of association. Thus, the contraction observed by the solution in water of 60 grams of acetic acid was found to be 5·8 c.c. Hence, the degree of association $= \frac{12·2}{5·8}$ $= 2·1$. In a similar manner, the degree of association of a large number of substances, organic and inorganic, has been obtained by Traube.[199]

The better known "co-volume method" makes use of the results mentioned in the preceding paragraph, together with a further discovery on the change of volume which occurs when a molecule of a substance is formed. According to Kopp, the molecular volume of any liquid may be represented as the sum of the atomic volumes of the atoms. Traube, from experiments in dilute aqueous solution, showed, however, that the molecular volume is greater than the sum of the true atomic volumes by an amount at 15°, of 13·5 c.c., that is to say, the formation of a molecule in dilute aqueous solution is attended by an increase in volume.

Now as it had already been found that a contraction occurs of 12·4 c.c.* when a gram molecule of a substance is dissolved in water, it follows that the homogeneous liquid has a molecular

* The original value of the contraction was 12·2 c.c. Subsequent experiments led to 12·4 c.c.

volume 13·5 + 12·4 = 25·9 c.c. (at 15°) greater than the sum of the atomic volumes of the elements. The molecular volume of the pure liquid may therefore be written :—

$$V_m = n\,9{\cdot}9\,C + p\,3{\cdot}1\,H + q\,1\,O' + r\,4\,O'' + \ldots\ 25{\cdot}9$$

where n, p, q, r, and s are the respective numbers of atoms of each kind, 9·9, 3·1, 2·3, and 5·5 are the true atomic volumes of the elements, O′ being hydroxylic oxygen, and O″ carbonyl.

More simply, the formula is

$$V_m = \frac{M}{d} = \Sigma\,(\text{At. Vol.}) + 25{\cdot}9$$

where d is the density. The equation expresses the fact that the volume occupied by a substance is the sum of the volume filled by the molecules and the space between the molecules (the co-volume).

The co-volume, 25·9, is an average number. For a very large number of unassociated substances, the value was found to range from 22-28.[200] A few substances of high molecular weight, and some tertiary compounds, have rather higher values, the co-volume of tri-*iso*butylamine being 37·1. When a substance is associated, the co-volume found is smaller than 25·9, if the molecular weight chosen for the substance is the normal value. By inserting the true molecular weight, xM, where x is the degree of association, the co-volume is restored to its true molecular value.

Hence the equation becomes

$$\frac{x\mathrm{M}}{d} = x\,\Sigma\,(\text{At. Vol.}) + 25{\cdot}9,$$

and x can be calculated by measuring the density at 15° and finding Σ (At. Vol.) from the table subjoined :—

Carbon	9·9	Chlorine	13·2
Hydrogen	3·1	Bromine	13·2
Oxygen (OH of COOH)	0·4	Iodine	13·2
Oxygen (OH)	2·3	Nitrogen (N‴)	1·5
Oxygen (CO)	5·5	Nitrogen (NO_2)	8·5-10·7

By this means Traube[201] arrived at values of x for a large number of liquids of which the following table contains a selection.

Substance.	x.	Substance.	x.
Water	3·06	Formic acid.	1·80
Methyl alcohol	1·79	Acetic acid	1·56
Ethyl alcohol	1·67	Propionic acid	1·46
iso-Propyl alcohol	1·66	Propionitrile	1·14
Glycol	1·88	Acetone	1·53
Glycerine	1·82	Phenol	1·43

The method, apart from any other criticism which may be levelled against it, has an obvious drawback in that a prior knowledge of the constitution of the substance is required before its molecular volume can be calculated.

Guye's Method.[202]

The existence of associated molecules in a vapour is regarded by Guye as proof of the complexity of the liquid and, on the basis of the law of mass action and the assumption that van der Waals' equation is applicable to a liquid provided no change of molecular condition occurs on condensation, he has deduced a method of measuring the extent of association.

The case treated was water, but this substance may be regarded as only a type of association represented by the formula

$$A_2 \rightleftarrows 2A.$$

It is presumed that this equilibrium exists both in the vapour and in the liquid; for the former, the molecular concentrations are connected thus,

$$C_2 = KC_1^2, \quad . \quad . \quad . \quad . \quad (1)$$

and for the latter,

$$C'_2 = K'(C'_1)^2, \quad . \quad . \quad . \quad (2)$$

where C_1 and C_2 and C'_1 and C'_2 are the concentrations of the single and double molecules respectively in the gaseous and liquid states, and K and K′ the respective equilibrium constants.

The question arises whether, knowing the quantities contained in the first equation, it is possible to investigate the second. If K may be substituted for K′, then the equation becomes

$$C'_2 = K(C_1')^2 \quad . \quad . \quad . \quad . \quad (3).$$

The arguments advanced in favour of the possibility of making this substitution are that it is possible to transform a vapour continuously into a liquid and that in the equilibrium $N_2O_4 \rightleftarrows 2NO_2$, the equilibrium factor remains constant for considerable changes in the specific volume. With this assumption made, let m_1 be the number of single water molecules, m_2 of double, in a unit volume of liquid. Then equation (3) becomes

$$m_2 = K(m_1)^2 \quad . \quad . \quad . \quad . \quad (4).$$

Now suppose this unit volume of water be converted at constant temperature into v c.c. of vapour containing n_1 single and n_2 double molecules.

Then the equation for the equilibrium in the vapour is

$$\frac{n_2}{v} = K\left(\frac{n_1}{v}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

since $\frac{n_1}{v}$ and $\frac{n_2}{v}$ represent the concentrations of the single and double forms.

Instead of dealing with the actual weight of water, suppose the weight of the single molecule be taken as unit, the mass being the same whether it is a molecule of gas or liquid. Then,

$$m_1 + 2m_2 = n_1 + 2n_2 = N \quad . \quad . \quad . \quad (6)$$

and if the degree of association of the liquid is x, then

$$x = \frac{m_1 + 2m_2}{m_1 + m_2} = \frac{N}{m_1 + m_2} \quad . \quad . \quad . \quad (7)$$

Also, the ratio of the weight of the single to that of the double gas molecules may be written y, where

$$y = \frac{n_1}{2n_2} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

From (4) and (6)

$$m_2 = K(N - 2m_2)^2$$

$$= \left(4NK + 1 - \frac{\sqrt{1 + 8NK}}{8K}\right), \text{ and}$$

$$m_1 = \left(-1 + \frac{\sqrt{1 + 8NK}}{4K}\right).$$

These values of m_1 and m_2 are now inserted in equation (7) so as to give x. The quantities N and K are got thus:—

$$\frac{n_2}{n_1} = K\frac{n_1}{v} \text{ by transformation of (5),}$$

and from (8), $\quad n_1 = \frac{v}{2Ky}$ and $n_2 = \frac{v}{4Ky^2}$.

Finally, $\quad x = \frac{2v(1 + y) - y^2 - y\sqrt{4v(1 + y) + y^2}}{v(1 + y) - 2y^2}$.

The degree of association can be obtained from the known specific volume v, and the degree of dissociation a of the double molecules of vapour, since $y = \frac{a}{1 - a}$.

For water the following values of x were calculated:—

Temperature.	a.	v.	x.
80°	0·913	3,285 c.c.	1·90
100°	0·911	1,582	1·86
120°	0·910	826·6	1·82

The value of v is measured under the pressure exerted by the vapour at the corresponding temperature.

The weakness of the method lies in the assumption that K can be substituted for K′ in the equation applying to the liquid; for van der Waals suggested that the equation bearing his name applied to the liquid only when no alteration of molecular complexity occurred during the transformation of state, and with water this is not fulfilled. Possibly also, molecules of greater complexity than double may be present, although the method might be extended to cover this case. The results, however, agree very well with those obtained at the same temperature by Walden (molecular cohesion method) and by Dutoit and Moijou.

The results also lead to the conclusion that whenever association occurs in the state of vapour, if only to the extent of 1 in 10,000, association will be appreciable in the liquid state. On the other hand, if a liquid is not associated, then no trace of association of the vapour molecules can occur.

Holmes' Method.[203]

Both the premises and the results of this method are very different from those already discussed. As a matter of fact, the determination of molecular complexity is based, not on the property of a liquid in the pure state, but by the volume changes which it undergoes when mixed with other liquids. In opposition to the views of many chemists, Holmes believes chemical changes to be rare when two liquids are mixed, the evolution and absorption of heat and change of volume all being supposed to be due to the agency of physical forces acting between the molecules.

The alteration of volume accompanying admixture of two liquids should, on the view that only physical forces are in evidence, be greatest in a mixture composed of equal numbers of each kind of molecule. This view can be made the subject of experimental test. The further assumption on which the method is based, is that the extent to which two liquids mix is governed in a large measure by the relative molecular volumes, or, what comes to the same thing, by the radii of these volumes, assumed to be spherical, in which the molecule exerts an influence.

In support of the first view, it was found that the maximum deviation between the calculated and observed volume of the

constituent of the mixture having the larger molecular volume (referred to the gaseous state) occurred either at equal or very simple molecular proportions. Thus, the maximum difference between the calculated and observed volume of alcohol in an aqueous solution is found when an equal number of alcohol and water molecules are present, and closely similar results are obtained when water is mixed with ethyl and propyl alcohols, formic, acetic and propionic acids and acetone. From these results, the conclusion was drawn that all these substances are of similar complexity, so that if the molecules of liquid water are normal in size, all the liquids named are normal; and if associated, the degree of association is the same. Hence follows the method of finding the relative degree of complexity of a liquid, namely, by mixing it with some other liquid capable of unlimited solubility and determining the composition of the liquid for which the greatest deviation occurs between the calculated and observed proportions by volume of the constituent with the greater molecular volume.

Water cannot be used as one constituent in many cases, but some liquid whose behaviour with water is already known may be employed. Thus, because the greatest deviation occurs with ether and alcohol when mixed in the proportion $(C_2H_5)_2O : C_2H_6O$, ether is regarded as of the same degree of complexity as alcohol and water. In turn, maximum deviations occur with mixtures of ether with benzene or chloroform at proportions $2C_6H_6 : (C_2H_5)_2O$ and $2\ CHCl_3 : (C_2H_5)_2O$ respectively, and benzene and chloroform are held to have double the degree of aggregation of ether.

The degree of complexity being only a relative value, some standard must be selected and ethyl tartrate was found to serve this purpose because this substance (and glycerol) has a lower degree of aggregation relative to water than other liquids tested. The deviations between the calculated and observed volumes of this ester in water are given below :—

Composition.	Deviation.
$C_8H_{14}O_6 \cdot H_2O$	0·842
$2H_2O$	1·181
$3H_2O$	1·325
$4H_2O$	1·379
$5H_2O$	1·362
$6H_2O$	1·330
$8H_2O$	1·205
$12H_2O$	0·974

The occurrence of the maximum deviation when the composition of the solution is given by $C_8H_{14}O_6 . 4H_2O$ is, on the theory, an indication that relative to ethyl tartrate, the water molecule is represented by $(H_2O)_4$.

By application of the process to other mixtures, the following table was drawn up. The temperature given is that at which the density of the mixture was determined.

Substance.	Temperature.	Degree of Complexity.
Glycerol	15°	$C_3H_8O_3$
Ethyl tartrate	15°	$C_8H_{14}O_6$
Nicotine	20°	$(C_{10}H_{14}N_2)_2$
Formic acid	20°	$(CH_2O_2)_4$
Acetic acid	15°	$(C_2H_4O_2)_4$
Propionic acid	25°	$(C_3H_6O_2)_4$
Methyl alcohol	15·5°	$(CH_4O)_4$
Ethyl alcohol	15·5°	$(C_2H_6O)_4$
n-Propyl alcohol	25°	$(C_3H_8O)_4$
Acetone	20°	$(C_3H_6O)_4$
Ethyl acetate	25°	$(C_4H_8O_2)_4$
Ethyl ether	25°	$(C_4H_{10}O)_4$
Methyl iodide	25°	$(CH_3I)_8$
Chloroform	20°	$(CHCl_3)_8$
Benzene	20°	$(C_6H_6)_8$
n-Hexane	17°	$(C_6H_{14})_8$
Carbon disulphide	15·5°	$(CS_2)_{16}$.

The results are almost entirely in opposition to those derived by methods based on physical theories and laws current in chemistry and have therefore been subjected to criticism.[204] Some of these difficulties will be clear from the discussion in the next section. Here two objections may be mentioned (1) that since the degree of complexity appears in all cases to be a whole number, then it is almost certain that the liquid cannot be a mixture of two or more types of molecule and further that temperature variation can produce no effect on the degree of association, especially since the liquids are not compared in corresponding states ; (2) the values of the degree of complexity are deduced from mixtures of liquids, and the degree of complexity appears to be independent of the second constituent of the mixture, a result wholly different from those based on measurements of the osmotic pressure or depression of freezing point. By the latter methods benzene, for example, has not given evidence of being of complex molecular character.

General Review of Methods and Results.

A general review of the many methods shows that there is a similarity between the state of a given substance in solution and in the liquid condition. As in solution, so also pure liquid substances containing the electro-negative groups OH, CONH, COOH, NOH, CN, NH_2 and CO, namely, water, the alcohols, phenols, amides and anilides, acids, oximes, nitriles, primary amines, and (certain) ketones, are associated, whilst fused salts, according to most methods, are still more associated.

Further, the degree of complexity is never represented by a whole number, so that, as in gases and solutions of associated substances, there must be at least two differently sized molecules. Moreover this degree of association varies with the temperature, decreasing as the temperature rises until, apparently, association disappears. From this circumstance, one may expect that heat is evolved by the association of liquid as of gaseous molecules.

All the above deductions can be made with much confidence; but which, if any, of the methods lead to the actual values of the degree of complexity is quite another matter. The extent of agreement may be tested by reference to substances, such as water, the alcohols and acids, which have been the subjects of tests by so many investigators, and the following table contains data for the comparison, the initials standing for the names of investigators previously mentioned in the text as devising the method.

DEGREE OF COMPLEXITY.

Substance.	R.-S.	R.-R.I.	B.	B.-M.	W_1.	W_2.	D.-M.	G.	L.
Water	2·66	1·405	1·10	—	1·98	2·57	1·96	1·82	4·6
Methyl alcohol	3·24	2·17	3·43	—	2·40	—	—	—	3·2
Ethyl alcohol	2·43	1·46	3·65	—	1·80	—	1·46	—	2·1
Formic acid	3·13	—	2·68	—	1·78	—	—	—	1·8
Acetic acid	2·9	1·79	2·74	—	1·95	—	—	—	1·7
n-Propylamine	1·24	—	—	1·20	—	—	—	—	1·5

The symbol $W._1$ represents Walden's molecular cohesion method applied at the boiling-point; $W._2$, the same worker's application of Trouton's Rule at the melting-point. It is not always possible to compare the values at the same temperature, but except that under $W._2$, all the results for water and the

alcohols are for the boiling-point temperature. Adopting water as the test substance it will be seen that the methods $W._1$, D.-M., and G. are in very fair agreement, but these apart, the degree of complexity varies between wide limits. For methyl alcohol, there is fair agreement between R.-S. and B., and between R.-R.I. and $W._1$; for ethyl alcohol between R.-R.I. and D.-M. and $W._1$ and L. It is therefore obvious that no great importance can be placed on the agreement between two or more methods for any one substance, as the same methods usually lead to different results when tested by a second substance.

In the absence of any guiding principle all that one can hope to do is to select the method against which fewest objections can be raised, and even here opinion is divided. Some methods must clearly be regarded as approximations, such as those depending on the use of melting-point as a corresponding temperature.

Of the surface tension methods the most satisfactory appear to be those of Walden and of Dutoit-Moijou based on specific cohesion. Bennett and Mitchell's method is still sounder in theory, but its results are rather difficult to explain in the light of solution measurements. But against surface tension methods in any form several objections have been raised, notably by Guye,[205] in whose opinion the molecular weight in the surface film is only the same as in the interior when the liquid is normal and not of high molecular weight; whilst if the liquid is associated, the degree of association will be greater in the liquid film owing to the powerful forces acting there. The methods most acceptable are, according to Guye, those which treat the liquid as a whole, like that of Traube or Longinescu. On the other hand, Tyrer[177] would reject surface tension methods, because they lead to results, in his opinion, too low; and, because they do not conform to the following conditions which any method must fulfil, he would also discard Ramsay and Shields', Ramsay-Rose-Innes', Batschinski's, Longinescu's, and Traube's methods:—

(1) The method must be based on a formula which contains a constant, the same for all substances, and be independent of the constitution.

(2) The formula must contain the molecular weight as one term.

(3) All the terms must be experimentally determinable and

must be related to the same molecular condition, or, if not capable of experimental determination, must be capable of deduction through differentiation or other suitable process.

4. All physical quantities must be independent of the number of associated molecular species existing in the liquid; or they must be strictly proportional to the association factor.

5. All the physical terms included in the equation must depend on the liquid as a whole and not on localized properties such as surface tension and vapour pressure; and they must either be independent of the vapour phase, or exist under conditions in which the vapour phase may be neglected.

Ramsay and Shields' method does not fulfil (1), (3), and (5); Batschinski's (3) and (5); Longinescu's (3), (4), and (5); Traube's (1). Only the method of Guye (chap. v.) applied at the critical point satisfies the conditions laid down, and this method is limited to a single temperature.

The objection which Tyrer considers vital is that the methods so far proposed are based on the comparison of the properties of a mixture of molecules X_1, X_2, and X_3 with a normal liquid of constitution X. But the only knowledge we possess at present depends on selecting some substance as standard and referring the abnormalities of other bodies to probable difference of molecular size; and whether the substances be gaseous, in solution, or liquid, there is no escape from the method.

There is one objection to present methods, however, different either from Guye's or Tyrer's, arising from a want of correspondence between solution measurements and those made on the liquid, an objection previously raised (p. 69) to accepting Bennett and Mitchell's results. The behaviour of alcohol is only one of many cases. In benzene its molecular weight, assuming the validity of Raoult's laws over the range of concentration tested, rises to seven times the normal value,[206] but no method applied to the pure liquid makes the degree of association to be more than about four. In solution the molecular weight rises with increasing concentration and it would be contrary to the law of mass action for a decrease in the degree of association to occur after a certain stage had been reached. Such a discrepancy naturally raises the question whether the values found for any liquid are multiples of the molecular weight in the ideal or gaseous condition, or only of the normal liquid. The actual value as-

signed to M in any equation applying to a normal liquid is that in the gaseous state. Ramsay [207] was inclined to think at first that the unit of molecular weight was different in the liquid and gaseous states, but modified this opinion in view of the fact that van der Waals' equation may be applied with considerable success to normal liquids, like pentane,[208] and the deduction made is that no change in the molecular state can therefore occur on transformation from gas to liquid.

On the other hand, some physicists regard the liquid state as essentially different from the gaseous in that when condensation occurs complex molecules are always produced; and doubt as to whether the molecular weight of normal liquids is that of the gas is even raised by recent work of van der Waals.[209] Both Garver [210] and Drucker [211] urge that the normal liquid is really composed of complex molecules. The normal substances, according to Drucker, are those in which the molecules are of a high degree of complexity and remain almost unaffected by temperature alteration, whilst associated substances consist of molecular complexes much more readily broken down. Almost precisely similar are the views of Schames,[212] according to whom the transition from the gaseous to the liquid, as also from the liquid to the solid, is always accompanied by a sharp change in the degree of molecular aggregation. This decision is arrived at by comparing the energy content of the substance before and after condensation at the same temperature. Both benzene and water, in the liquid state, are associated and at each change of state the degree of aggregation is doubled. Near the point of condensation, the saturated vapour of benzene is calculated (at 80°) to have 16·3 per cent of double molecules whilst the liquid itself corresponds to $(C_6H_6)_2$. Near the freezing-point $(C_6H_6)_4$ molecules begin to appear, the solid consisting of $(C_6H_6)_4$. Liquid water, again, is supposed to contain $(H_2O)_3$ and $(H_2O)_6$; ice $(H_2O)_6$ and $(H_2O)_{12}$, the more complex molecules in each case increasing in proportion with fall of temperature. Water is supposed to differ from benzene in that it consists, at every temperature, of a mixture of different molecules, whereas with benzene, a type of the so-called normal substance, a mixture is only obtained in the neighbourhood of the change points.

These views, if true, would undoubtedly clear up some of the difficulties arising from a consideration of the results of the various

determinations of the degree of molecular complexity of liquids, but, at present, they can be said only to have reached the suggestion stage. In view of the great influence which van der Waals' equation and its applications have had and still have on our conceptions of condensation and allied phenomena, it is certain that the newer views mentioned will receive the closest scrutiny before being accepted. Undoubtedly before any real advance can be made in our knowledge of the liquid state, we must have first a clear conception of the phenomenon of condensation, particularly in regard to any molecular change that occurs. To accumulate empirical methods of testing liquids is fruitless.

CHAPTER VIII.

THE MOLECULAR COMPLEXITY OF WATER AND THE THEORY OF DYNAMIC ALLOTROPY.

THE great importance of water as a solvent makes a study of its molecular state of particular interest. Whatever its condition as a liquid, its vapour density is not very far removed from the normal and, until recently, the existence of complex vapour molecules had not been recognized, although the vapour densities previously determined were known to contain slight abnormalities. The explanation of these, Bose [213] showed, was due to a small percentage of double molecules in the saturated vapour; for the vapour density results of Kornatz [214] could be accurately expressed by the formula

$$d_t = d_o - \frac{K}{P}\left[\sqrt{1 + \frac{d_t P}{K}} - 1\right] \text{ (\textit{vide footnote}, p. 19).}$$

d_o was taken to be 1·2432, the value of the density if all the molecules were double. From the density values, the degree of dissociation (α) of the double molecules at various temperatures and under the pressure of the vapour at the corresponding temperature were:—

Temperature.	P (Vap. Pressure).	α.
0°	4·579 mm.	0·934
50°	92·17 ,,	0·918
100°	760·00 ,,	0·911
150°	3581 ,,	0·910
200°	11688 ,,	0·913

Evidently the dissociating effect of rise of temperature is counterbalanced by the increasing pressure, so that the molecular state remains practically the same over a wide range.

In the state of solution, this tendency to form complex molecules proceeds distinctly further, as illustrated by the following results in various solvents

Solvent.	Concentration.	M.W. (H_2O = 18).
p-Toluidine [215]	0·452 -1·602	28·7-33·3
Phenol [215]	0·903 -1·329	19·4-19·6
Bromoform [139]	0·0105-0·0196	18·9-23·5
Methyl oxalate [139]	0·0825-1·820	20·6-35·9
Veratrol [139]	0·0539-2·13	17·6-30·0

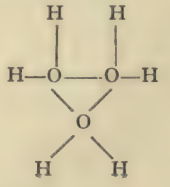
The fact that liquid water molecules are complex has already been indicated by the many methods described in the preceding three chapters, but there are still other abnormal properties of water, such as melting-point and latent heat of fusion, thermal expansion, specific heat, optical refraction,[216] compressibility, viscosity, dielectric constant,[217] colour and coefficient of magnetization,[218] which afford additional evidence of its abnormal molecular condition.

All the established methods of measurement lead to non-integral values of the factor of association, indicating that two or more molecular forms exist side by side. Before any means of determining association in liquids had been devised, however, Röntgen [219] had suggested that all the abnormal properties of water could, qualitatively, be readily accounted for by supposing liquid water to be a saturated solution of ice in some other form of water. These views have been taken up by Sutherland,[220] who has endeavoured to prove that steam is represented by H_2O, termed hydrol, ice by $(H_2O)_3$, trihydrol, liquid water being a mixture of tri- and dihydrol, $(H_2O)_2$. From the abnormal specific heat, for example, the percentage of trihydrol in liquid water was calculated to be

Temperature	0°	20°	40°	60°	80°	100°	120°	140°	198°
$(H_2O)_3$ per cent	37·5	32·1	28·4	25·5	23·4	21·7	20·3	19·1	16·5.

The gradual decrease of trihydrol is believed to have its upper limit at the critical point, when water becomes pure dihydrol.

Steam, as already mentioned, has recently been shown to contain some double molecules. At the other end of the scale the triple molecules supposed to constitute ordinary ice, are also supposed to bestow on it its characteristic hexagonal crystalline form through the combination of the oxygen atoms producing a symmetrical molecule.



When water combines with salts, it is supposed by Sutherland to be present as hydrol, because in $LiSO_4\ H_2O$, with a single molecule of water, the 18 grams of water occupy a volume, according to density measurements, of 13·3 c.c., much the same as that found for thirty-one other salts containing water of crystallization, in which the mean value is 13·76 c.c. Hence, the density of hydrol when solid is $\frac{18}{13{\cdot}76} = 1{\cdot}31$. As ice has a density of 0·917 at 0° and water is a mixture of di- and trihydrol, the density of pure dihydrol may be calculated from the known density of water.

The degree of complexity of liquid water is supposed, according to the same theory, to be altered not only by temperature variation but also when it acts as a solvent, a positive ion converting tri- into dihydrol, and a negative ion causing a reversal of this change; and the failure of the mixture law for the specific heat and surface tension of aqueous solutions is supposed to be due to this transformation of the molecules of solvent in this way.

In somewhat the same manner, Armstrong[221] has attempted to explain the phenomena of aqueous solutions as due less to the solute than the solvent. Instead of limiting the aggregates to groups of three single molecules, rings or chains of molecules may be formed. Of the various types, H_2O, hydrone, and $HO\begin{matrix}H\\ \diagdown\\ \diagup\\ OH\end{matrix}$, hydronal, are active forms of water, whilst the complexes $H_2O : OH_2$, $H_2O{-}OH_2$ ($\diagdown\diagup OH_2$), $H_2O{-}OH_2$ ($|\ H_2O{-}OH_2$) and so on, are inactive; and the main effect of the solute, it is assumed, is the inter-conversion of and combination of the substance with the various forms.

Bousfield and Lowry[222] similarly suggest that at moderate temperatures water is a mixture of ice and water molecules, and near its boiling-point, of steam and water molecules, so that water may be a ternary mixture.

Although ordinary ice is the hexagonal form, experiments on the formation of ice under pressure has led to the discovery of several different forms, five stable forms now being definitely recognized. The new forms are denser than ordinary ice, and

Tammann[223] regards the differences between the various forms as due to different molecular types.

The Theory of Dynamic Allotropy.

The fact that molecules of different kinds can coexist in any liquid, the proportion of each depending on the temperature and other factors, has paved the way for a new view of allotropic modifications, according to which both forms can be present in a state of equilibrium. This theory has arisen more particularly as a result of the study of liquid sulphur,[224] the abnormal behaviour of which has been demonstrated to be due to a mixture of a mobile, yellow liquid called S_λ, which predominates in amount, and a viscous brown liquid S_μ the proportion of which increases with rise of temperature and attains a proportion of 40 per cent at the boiling-point, 445°. The two forms are further distinguished and rendered separable, and therefore capable of determination, by the fact that S_λ is soluble, whilst S_μ is insoluble in carbon disulphide; S_μ, indeed, corresponds in the quasi-solid form to the well-known amorphous sulphur. Certain reagents have the effect of stimulating the rate at which the equilibrium between the two forms is attained at a given temperature, other reagents retard the rate. Ammonia is such a stimulant, sulphur dioxide a retarder, and by the addition of the latter, the mixture can be cooled and afterwards analysed without the equilibrium set up at the higher temperature being disturbed. Sudden cooling by plunging into cold water will also retard the change and preserve the equilibrium proportions. By such a method, Smith and Carson[224] obtained the following proportions of the two varieties:—

Temperature . .	121°	154°	156°	162°	165°	167°
S_μ per cent . .	3·75	7·5	8·0	13·5	15·5	16·7

When monoclinic sulphur melts, therefore, it gives rise to two liquid forms, so that at the melting-point (solid) monoclinic sulphur, the two liquid forms S_λ and S_μ and vapour are all present in equilibrium. The temperature at which the first three are present together under atmospheric pressure is termed the natural freezing-point of monoclinic sulphur, and its value, according to Smith and Carson,[225] is 114·25°, S_μ to the extent of 3·6 per cent being present. Monoclinic sulphur, which is regarded as the solidified S_λ, has, when pure, a higher freezing-point, 119·25° according to Smith

and Carson, or 118·95° according to Wigand. The freezing-point was obtained by the analysis of samples of sulphur which had been heated for varying periods, thereby lowering the freezing-point according to the amount of S_μ produced, and extrapolating the temperature of freezing to the point at which $S_\mu = 0$. When this freezing-point of pure monoclinic sulphur had been fixed, it was possible to calculate the molecular weight of S_μ from the known depression of freezing-point produced by known quantities present. The atomic depression, that is the lowering of freezing-point by the solution of 32 grams of S_μ in 100 grams of S_λ, was thus found to be 46·1. Using Person's value of the latent heat of fusion, l, 9·368, the atomic depression calculated from van't Hoff's equation $C = \frac{0{\cdot}0198\ T^2}{l}$ was 325°, which is 7·6 times the observed value. Hence Smith and Holmes concluded that the molecular weight of S_μ, like that of S_λ, corresponds to S_8, and that the change which accompanies the conversion of one form into the other is intramolecular.

As the value of the molecular size depends on the latent heat of fusion employed, Smith's result has been subjected to revision. Thus Tammann found $l = 12{\cdot}5$ and the number of atoms 5·74, or, S_μ is S_6; Wigand [224] found $l = 10{\cdot}4$, and the number of atoms 6·9, and considering this value somewhat low, concluded that S_μ is S_8. Smith and Carson [225] using Lewis and Randall's [226] value for the latent heat of fusion, subsequently identified S_μ with S_6, as also did Beckmann [226a] independently.

This work on the nature of liquid sulphur, coupled with the previously stated views on water, another substance which must be regarded as exhibiting this dynamic allotropy, may have considerable influence on the subject of molecular association along two lines. In the first place it may be possible, as with water and sulphur, to trace the change of molecular condition, if any, through from the gaseous to the solid state. Although it had no stated reference to the theory of dynamic allotropy, Guye's method marks one such attempt since the degree of association of a liquid is determined from the known association in the vapour state. A somewhat different example, and one more clearly illustrating the point, is Preuner and Schupp's [10] investigation of liquid sulphur. These investigators believed that S_μ has the molecular formula S_6 and is identical with the vapour

molecule S_6 already shown to exist in conjunction with S_8 at temperatures near and below the boiling-point. In order to test this view, they calculated from the equilibrium formulæ given in chap. II. the proportion of S_6 present at different temperatures and compared the results with the amounts of S_μ found by Gals.[227] Fairly good agreement was found between the values of Gals and those calculated from the partial pressures of S_6 in the vapour. Thus:—

Temperature	215°	230°	245°	260°	290°	320°
Per cent S_μ (Gals.)	18	22	25	28	34	37
Per cent S_6 (P. and S.)	20	22	24	25	30	34

A further attempt, in this case, to connect the liquid and the solid state, has been made by Tammann,[228] based on the coefficient of surface energy of the liquid substance. If a vapour contains molecules of different kinds, then the liquid formed on condensation should be associated and a mixture of two or more molecular species; so also, when the liquid is converted into a solid, the different liquid molecules may be expected to give rise, as a rule, to different crystalline forms. In the main, Tammann finds this is true, that normal liquids only give rise to a single crystal group, whilst the associated give rise in most cases to two stable groups. The test of association is the value of the coefficient of molecular surface energy, association being presumed if $k < 2{\cdot}00$. Thus:—

Substance.	No. of crystal groups.	No. of unstable forms.	k.
Water	2	2	0·88
Acetic acid	2		0·90
Formic acid	1	4	0·90
Sulphur	2		1·51
Phenol	2		1·80
Nitrobenzene	1		2·23
p-Cresol	1		2·24
Acetophenone	1		2·40
Diphenylamine	1		2·62
Veratrol	1		2·97

In this way we have the different molecular species preserving their individuality through changes of state, the only effect being an alteration of the proportions of each.

The idea of dynamic allotropy, as with liquid sulphur, has been extended to liquid phosphorus,[229] and attempts, less successful, have been made to apply the theory even to the solid form of the element.[230] Benedicks,[231] again, sees in the fact that the

transition point of silver iodide varies over a range of temperature in the neighbourhood of 147°, evidence of the co-existence of two solid forms, mutually soluble and in equilibrium; and he has extended the same mode of explanation to the allotropic forms of iron, reviving the earlier theory of Osmond and Werth that iron exists in two forms only, the present α and γ forms, and that β iron is only a solid solution of these two forms. Further, it has been suggested that the existence of different forms of tin may be due to a similar cause, as also the existence of two phases, the hard and soft states, which many metals can possess.[232] It is well to bear in mind, however, that these are not cases which can be explained on the basis of the existence of dynamic allotropy in the liquid state, for as already shown in preceding chapters, the liquid metals appear to be monatomic.

The second possible effect of the theory on the study of molecular association lies in the investigation of the effect on the solvent of added substances. The experiments on liquid sulphur have brought to light the fact that certain reagents, such as ammonia, may assist in establishing equilibrium between the different molecular varieties; others, like sulphur dioxide, may retard; whilst others still, like iodine, may even displace the point of balance. If this is so with sulphur, there seems no reason why it should not occur with water or other complex liquids when solutes are added, in some such way as already suggested by Sutherland, Armstrong, Bousfield and Lowry, Drucker and Kassel, and the writer (see chap. IV.), all from independent points of view. Very few direct tests of such a possibility have been made.

CHAPTER IX.

THE SELECTION AND USE OF MOLECULAR FORMULÆ.

In order to ascribe a formula to a substance, its composition and the atomic weights of the constituent elements must be known. When known, the simplest possible formula can be calculated and the molecular formula can be obtained by comparing the simplest formula weight with the molecular weight derived by applying Avogadro's hypothesis.

Avogadro's hypothesis requires the comparison of the standard gas and the gas of unknown molecular weight to be carried out under the same conditions of temperature and pressure. As no two gases alter in volume in precisely the same way when heated or compressed, the comparison is carried out either at zero pressure or at a high temperature, and the relative densities then reduced to 0° and 760 mm. (and latitude 45°); or, what comes to the same thing, the deviations from the gas laws between zero pressure and 760 mm., or between 0° and the comparison temperature may be determined and a correction introduced.

The number of accurate molecular weights that can be so deduced is very small; but the molecular formula of a substance can be obtained from an approximate molecular weight determination. Although this approximate method provides molecular formulæ for many substances, there are two classes which create special difficulty, (1) those which cannot be vaporized, (2) those whose molecular size varies with the temperature and pressure.

The first class comprises a very large number of substances, in fact, the majority of known substances. When formulæ such as $NaOH$, Na_2O, KNO_3, $CaSO_4$, etc., as well as those of many organic substances, are written down it must be remembered that they may not, in fact, very likely do not, represent molecular quantities, but are only empirical. The true formulæ are $(NaOH)_n$, $(KNO_3)_n$ and so on, where n is yet unknown. Struc-

tural formulæ both in inorganic and organic chemistry are written for many substances the molecular weights of which are not known, and although much help in studying chemical reactions is often to be gained from their use, it has to be borne in mind that they can only be tentative so long as the molecular formula remains unknown.

The second class of substances illustrates the fact, clearly brought out in the preceding pages, that the molecular weight of a substance is to be regarded as a physical property, dependent, like other properties, on the conditions of temperature, pressure and surroundings. Even for the permanent gases, comparison at 0° and 760 mm. is not easy because of the difficulty of obtaining "the same conditions of temperature and pressure"; and with substances which change their molecular size according to the conditions imposed, the selection of a single formula is obviously impossible. In such cases, the molecular formula selected has usually been the simplest one, on the ground that rise of temperature tends to produce the single molecule. Thus, Biltz and Meyer,[38] when determining the molecular weight of stannous chloride, found the density changed from 8·76 to 7·08 (relative to air) between 639° and 1113°. As the value corresponding to $SnCl_2$ was 6·53, the investigators named came to the conclusion "dass Zinnchlorürdampf mit Molekülen von der Formel Sn_2Cl_4 in der That nicht existiert". The obvious conclusion is rather that a mixture of molecules $SnCl_2$ and Sn_2Cl_4 exists over the above range of temperature.

The habit of adopting the limiting value of the formula, or that which seems most likely at high temperatures does not, however, appear to have been very consistently followed. Thus, although stannous chloride, aluminium chloride, and acetic acid are usually written as $SnCl_2$, $AlCl_3$, and CH_3COOH respectively, arsenious oxide and iodine are most often written As_4O_6 and I_2, although in both cases rise of temperature ultimately brings about complete dissociation. Vapour density determinations carried out in the last few years make it clear that most molecular formulæ for elements should, if chosen as above, correspond to the atom. Thus, iodine, bromine, and (apparently) chlorine, sulphur, selenium, hydrogen may all be represented by monatomic molecular formulæ I, Br, Cl, S, Se, and H, and it is most probably only a matter of overcoming experimental difficulties before all elements are reduced to the monatomic state.

The extension of the gas laws to solutions provides a means of testing a large number of the substances belonging to the first class above, namely, the unvaporizable substances, but greater care needs to be taken in interpreting the results than has been observed in the past. In the state of vapour, the factors which may modify the density are the temperature and the pressure. In Meyer's method of finding the density a filling gas is employed, but it is always chosen so as to be chemically indifferent to the vaporized substance. Further, the dielectric constant of a gas or vapour is only so very little greater than unity (vacuum = 1) as to be without effect in modifying the forces acting within the molecule. In a solution, the modifying factors are temperature, concentration, and medium, and if vapour density measurements are to be comparable with solution measurements, the following conditions ought to be observed :—

(*a*) Reduction of the molecular weight to the temperature of 0°. (*b*) The standard solution should be that which exerts an osmotic pressure of one atmosphere. (*c*) The dielectric constant should be low.

It is obviously not easy to fulfil condition (*a*), but (*b*) can more easily be adopted. In addition to (*c*), care ought to be taken that the solvent shall have no chemical influence on the solute, just as the filling gas in Meyer's method must be an indifferent one. No one would accept vapour density determinations by Meyer's method if oxygen or chlorine was the filling gas. Yet the necessity of this factor is often over-looked in solution measurements, and wrong interpretations of molecular weight results have often been made. Thus, cuprous chloride both in bismuth[233] chloride and in pyridine[120] appears to have the formula CuCl. In bismuth chloride the result is undoubtedly due largely to the high dielectric constant of the solvent; in pyridine, combination with the solvent to form a compound $Cu_2Cl_2 . 6\ C_5H_5N$[234] occurs, and the experiment, as a molecular weight determination, ought to be ruled out. The same objection, namely that chemical action occurs, may also be raised to certain of Beckmann's determinations such as those of the molecular weights of a number of metallic salts in quinoline.[235] In the state of vapour, no distinct reduction below the formula Cu_2Cl_2 has so far been obtained, and this formula is probably more truly representative of the molecular state of cuprous chloride than the result of the

determination in bismuth chloride, owing to the modifying effect of the dielectric character of this solvent.

From what has been said, the difficulty of obtaining really representative molecular formulæ will be evident. There are several conceivable ways of deriving such formulæ:—

1. Abandon solution measurements and rely on vapour density determinations only, as in the original application of Avogadro's hypothesis, but carry out the comparison of densities at a temperature within 100° of the boiling-point, since this is roughly a corresponding state for different liquids.

2. Rely only on vapour density determinations and select as molecular formula the value corresponding to the limiting density obtainable at high temperatures.

3. Make the molecular formula correspond to the particular conditions under which the substance exists.

Obviously (1) and (2) are only compromises. Nothing has yet been said in this chapter of the molecular formulæ of liquids and solids, but (3) takes these states into account. However difficult of attainment, (3) is the only theoretically sound method. It requires that the formula of a substance shall be recognized as a function of the physical conditions under which it exists, so that the formula for elements is X_n, for compounds $(XY)_n$, where n is to be specified according to the conditions. Although we are far from realizing how n varies for most substances, the adoption of such formulæ would bring home clearly the fact that both the physical and the chemical behaviour of a substance may be closely dependent on the value of n.

CHAPTER X.

MOLECULAR ASSOCIATION AND PHYSICAL PROPERTIES.

As shown in preceding chapters, the marked effect which association has on the physical properties of a substance has been employed to provide methods both of detecting and measuring the extent of association. Reference has been made to the abnormal osmotic pressure, lowering of vapour pressure and freezing point, latent heat of evaporation and fusion, thermal expansion and specific heat, critical temperature and the critical ratios, surface tension and surface energy, and viscosity and fluidity. There are still other properties which association has been found to affect, although to an extent which is not sufficiently well marked as to serve, in turn, as a means of detecting association. Several such properties are discussed in this chapter.

Degree of Association and Dielectric Constant of a Liquid.

On the whole, these two properties run parallel, substances strongly associated having, with few exceptions, high dielectric constants. The converse of this is not true, for a number of substances of high dielectric constant are unassociated. These facts are brought out in the following table.[235a] In the absence of any reliable method widely applied in the determination of degree of association, the association factors obtained by use of the Ramsay and Shields' method are inserted. Too great a value must not be attached to them.

Substance.	Association Factor.	Dielectric Constant.
Formamide	6·18	>84
Ethylene cyanide	>7·3	61·2
Water	3·81	81·7
Formic acid	3·61	58
Acetic acid	3·62	6·3
Methyl alcohol	3·43	32·5
Ethylene glycol	2·92	41·2
Ethyl alcohol	2·74	26·0
Acetamide	2·47	59·2
Propyl alcohol	2·25	22·2

Substance.	Association Factor.	Dielectric Constant.
Lactonitrile	2·21	37·7
iso-Amyl alcohol	1·97	16·0
Acetonitrile	1·73	38·8
Formanilide	1·69	20·5
Nitromethane	>1·59	38·2
Propionitrile	1·48	27·5
Butyronitrile	1·38	20·3
Dimethylnitrosoamine	1·34	53·3
Acetone	1·26	21·2
Acetanilide	1·21	19·5
Acetyl chloride	1·06	15·5
Ethyl thiocyanate	1·04	19·5
Benzylnitrile	1·03	18·2
Phosphorus trichloride	1·02	4·7
Carbon tetrachloride	1·01	2·25
Ethyl iodide	1·01	7·4
Benzene	1·01	2·3
Acetic anhydride	0·99	20·7
Ether	0·99	4·3
Benzaldehyde	0·97	14·5
Sulphur monochloride	0·95	4·8
Nitrobenzene	0·93	35·5

It may be remarked that Dutoit and Moijou find nitrobenzene and benzonitrile slightly associated.

Solvent Power and Degree of Association.

Belief in the dependence of solubility on the molecular state has been expressed by a number of observers. One of the first was Crompton,[236] who pointed out that unimolecular liquids mixed readily, but the mutual solubility of unimolecular and associated substances is, as a rule, limited. Walden[237] also found that the solubility of a salt, tetraethylammonium iodide, was distinctly dependent on the degree of association of the solvent. In the following table the degree of association is again that derived from Ramsay and Shields' method and the solubility is the amount of salt per 100 c.c. of solvent.

Solvent.	Solubility at 25°.	Degree of Association.
Water	35·5	3·6
Methyl alcohol	10·7	3·43
Glycol	7·55	2·92
Nitromethane	5·94	1·59
Acetonitrile	3·04	1·73
Ethyl alcohol	0·88	2·74
Propionitrile	0·81	1·48
Ethyl *iso*-thiocyanate	0·475	1·16
Benzonitrile	0·467	1·02
Acetone	0·249	1·25
Ethyl acetate	0·0004	0·99

Associated substances like formamide, formic and acetic acids, and phenol also readily dissolve this and similar salts, whilst non-associated liquids as ether, benzene, ethylene dibromide, carbon disulphide do not.

Crompton's views have been extended by the writer,[238] who has indicated that a substance is associated, as a rule, only in the solvents in which its solubility is rather limited. Thus, speaking broadly, hydroxyl-containing substances, amides and their derivatives, oximes, nitriles and salts are but slightly soluble in the hydrocarbons and their halogen derivatives, in which association is exhibited. An attempt to obtain a quantitative relationship, however, has not so far succeeded.[239]

The belief in the relationship between degree of association and solubility has been carried much farther by Holmes, so far, indeed, as to base a method of determining relative association factors on the extent of miscibility (see chap. VII.)

Electrical Conductivity and Degree of Association.

Under this heading may be included both the power of forming a conducting medium and of acting as an electrolyte in solution.

Associated liquids when acting as solvents usually form good conducting media, and also possess a distinct or high conductivity when pure. Organic liquids certainly cannot be compared with inorganic in this respect, but of the five best conducting liquids found by Walden,[240] namely,

Substance.	Formamide.	Acetamide.	Dimethylnitrosoamine.	Acetylacetone.	Formic Acid.
Sp. Conductivity	$4{\cdot}7 \times 10^{-5}$	29×10^{-5}	3×10^{-5}	$1{\cdot}6 \times 10^{-5}$	$1{\cdot}5 \times 10^{-5}$

only acetylacetone is non-associated. The conductivity of inorganic halogen-containing compounds is likewise great when the degree of association is highest and drops to zero with non-associated substances. In the following table, the substances are arranged in the order of their degree of association. K represents the specific conductivity.[241].

Substance.	κ.	Substance.	κ.
Sodium chloride	3·34 (750°)	Sulphuryl chloride	$0{\cdot}18 \times 10^{-6}$
Potassium chloride	1·91 (750°)	Arsenic trichloride	$1{\cdot}24 \times 10^{-6}$
Lead chloride	2·39 (520°)	Tin tetrachloride	Nil.
Silver chloride	1·83 (500°)	Antimony pentachloride	Nil.
Antimony chloride	109×10^{-6} (80°)	Silicon tetrachloride	Nil.
Phosphorus oxychloride	$2{\cdot}2 \times 10^{-6}$	Phosphorus trichloride	Nil.
Thionyl chloride	$2{\cdot}0 \times 10^{-6}$		

The conductivity of an electrolyte also depends to a considerable extent on the degree of association of the solvent.[240] This follows from the connexion already shown to exist between association factor and dielectric constant, for on the latter property the conductivity of a solution closely depends. As there are many exceptions to the parallelism between association factor and dielectric constant, so likewise the association factor of the solvent does not control the conductivity of the solution.

Inorganic electrolytes are, as a class, associated substances. This statement applies to salts and acids * for, as yet, nothing is known of the molecular condition of bases. Even organic electrolytes are most often associated bodies. Thus, when dissolved in the liquefied halogen haloids, organic acids, alcohols, phenols, amides, and nitriles conduct a current, although ether and thymol, unassociated substances, behave similarly.[242] Although but qualitative, the connexion between association and conductivity and association and ionizing power seems so certain, that of about one hundred associated substances of all types, all have been found to possess a distinct conductivity, or to exert ionizing power, or both.[77]

In solvents of low dielectric constant, the highly complex molecular state of salts must be taken into account in attempting to explain the conductivity of the solution. An interesting example, in this connexion, is furnished by Isbekow's work [87] on aluminium bromide as a solvent, in which non-conducting haloid bodies, such as phosphorus trichloride, were found to be non-associated; whilst salts, like bismuth tribromide, producing conducting solutions, were strongly associated. The molecular conductivity of the salt solutions increased as the concentration increased, so that the ions cannot be of the same type as those which are assumed to carry the current in aqueous solution.

Molecular Association and Optical Rotation.

The effect of the solvent on the rotation of an optically active substance has been the subject of repeated investigation. As the outcome of an extended review of the subject, Walden [243] came to the conclusions that (1) There exists a connexion between the osmotically determined molecular size of the active solute and its

* The term acid refers here to the dry substance.

rotation in the same solvent, (2) The relationship between the degree of association and the rotation is not, however, revealed in a simple parallelism, but each constituent of the solution exercises constitutive influences on the value of the rotation.

The substances used by Walden in the test were dimethyltartrate, diethyltartrate, dimethylmalate, diethylmalate, and dimethylacetylmalate. With dimethyltartrate the following results were obtained :—

Solvent.	Benzene.	Et. Acetate.	Acetone.	Me. Alcohol.	Acetonitrile.	Chloroform.
M.W.	305	219	195	183	173	253
$[\alpha]_D$	− 1·7	+ 2·6	+ 5·8	+ 6·7	+ 10·8	− 6·2

The molecular weight calculated from the simple formula is 178·1, and it will be seen that as the observed molecular weight increases, the rotation falls. As chloroform does not fall into line, and as, moreover, a substance may cause different rotations in solvents in which its molecular weight is normal, it is evident that association cannot be the factor controlling the rotation.[244]

Other evidence of the influence of molecular size on optical activity has been obtained by Navassart[245] who found that the rotation of tannic acid in different solvents appears to decrease as the molecular size of the solute increases.

CHAPTER XI.

MOLECULAR ASSOCIATION AND CHEMICAL COMBINATION.

In seeking to trace the nature of the forces which cause the molecules of so many substances to form aggregates, one naturally contrasts association with chemical combination. In both phenomena there is attraction between molecules, in the first attraction between like, in the second between unlike molecules. This apparent similarity has, indeed, led several chemists to propound "association" theories of chemical action. When two bodies react, according to this view, at least two stages are passed through. There is first of all a union (or association) of the two molecules resulting in a molecular compound which is not stable, so that a rearrangement of the atoms proceeds with the production either of a new type of molecule or of two or more molecules. Kekulé [246] was the propounder of such a view. H. E. Armstrong [247] explained the oxidation of hydrocarbons in a similar manner whilst Engler [248] suggests that the first stage of all oxidations by oxygen is the association of the oxygen molecule as a whole with the substance being oxidized. The solution of ammonia in water is also supposed to result first in the formation of $NH_3 . xH_2O$, part of which is then transformed into the hydroxide NH_4OH.[249] The test of such a hypothesis as Guye [250] pointed out, can readily be made in connexion with many reactions between organic bodies, by investigating their freezing points when mixed, since at such temperatures the reaction is usually exceedingly slow. By a study of their equilibrium diagrams, Wroczynski and Guye [250a] and Schmidlin and Lang [250b] have found direct confirmation of this view of the mode of chemical action between a number of organic substances.

Belief in the similarity of molecular association and chemical action also finds expression in the structural formulæ which have been proposed for associations or aggregations of similar

molecules. Water and hydroxyl-containing molecules are supposed to form aggregates through oxygen acting as connecting link (see chap. VIII.); whilst for the sulphur molecule, one of the three following formulæ is supposed to represent it [250c], according as the sulphur atom is assumed to be di-, tetra-, or hexavalent.

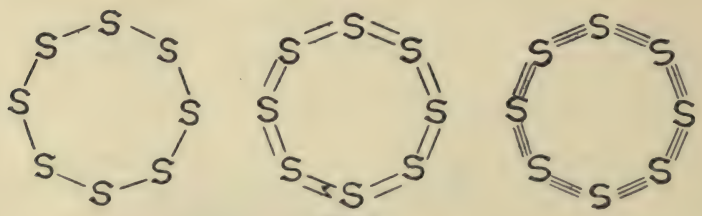


FIG. 6.

The best way of illustrating the relation between association and chemical combination is, perhaps, to consider the properties of the components from which molecular compounds are formed. For this purpose the following list, containing, in the main, substances which are associated, has been drawn up. Each pair is only a type of many similar ones.

Constituents.	Compounds Formed.
Hydrogen iodide : Water [251]	$HI.3H_2O$; $HI.2H_2O$
Nitric acid : Water [252]	$HNO_3.2H_2O$; $HNO_3.H_2O$.
Potassium hydroxide : Water [253]	$KHO.H_2O$; $KHO.2H_2O$; $KHO.4H_2O$
Ammonia : Water [254]	$NH_3.H_2O$; $2NH_3.H_2O$
Lithium iodide : Water [255]	$LiI.3H_2O$; $Li.H_2O$.
Lithium iodide : Me. alcohol [256]	$LiI.3CH_3OH$
Lithium iodide : Et. alcohol [256]	$LiI.4C_2H_5OH$
Lithium iodide : Pr. alcohol [256]	$LiI.4C_3H_7OH$
Lithium iodide : *iso*-Am. alcohol [256]	$LiI.4C_5H_{11}OH$
Hydrogen bromide : Pr. alcohol [257]	$2HBr.C_3H_7OH$
Lithium iodide : Acetic acid [256]	$LiI.3CH_3COOH$
Hydrogen chloride : Formamide [258]	$3HCl : H.CONH_2$.
Sodium iodide : Acetamide [259]	$NaI.2CH_3.CONH_2$
Lithium chloride : Ethylamine [260]	$LiCl.C_2H_5NH_2$; $LiCl.2C_2H_5NH_2$; $LiCl.3C_2H_5NH_2$
Magnesium iodide : Et. carbamate [261]	$MgI_2.6NH_2.COOC_2H_5$
Magnesium bromide : Urea [261]	$MgBr_2.6CO(NH_2)_2$.
Magnesium iodide : Acetonitrile [262]	$MgI_2.6CH_3CN$
Magnesium bromide : Acetone [262]	$MgBr_2.3(CH_3)_2CO$.
Magnesium Iodide : Ammonia [263]	$MgI_2.6NH_3$.
Phenol : Urea [264]	$C_6H_5OH.2CO(NH_2)_2$.
p-Cresol : Aniline [264]	$C_6H_4CH_3OH.C_6H_5NH_2$.
Phenol : a-Naphthylamine [264]	$C_6H_5OH.C_{10}H_7NH_2$.
Resorcinol : *p*-Toluidine [265]	$C_6H_4(OH)_2.C_6H_4CH_3NH_2$
Catechol : α-Naphthylamine [265]	$C_6H_4(OH)_2.C_{10}H_7NH_2$.

Constituents.	Compounds Formed.
Aniline : Et . acetate [248]	$C_6H_5NH_2 . CH_3COOC_2H_5$; $3C_6H_5NH_2 . 2CH_3 COOC_2H_5$; $2C_6 H_5 NH_2 . CH_3 COOC_2H_5$
Phenol : Acetone [249]	$2C_6H_5OH . (CH_3)_2CO$.
Resorcinol : Acetone [249]	$C_6H_4(OH)_2 . 2(CH_3)_2CO$.
Phenol : Cyclohexanone [249]	$C_6H_5OH . C_6H_8O$.
l- and *d*-Dimethyltartrates [266]	$C_6H_{10}O_6 . C_6H_{10}O_6$.
Urea : *p*-Nitrophenol [267]	$CO(NH_2)_2 . C_6H_4NO_2 . OH$.

Ethyl acetate and α-naphthylamine are the only substances which are doubtfully associated; magnesium bromide and iodide have not been tested but are probably associated.

Hundreds of molecular compounds formed from constituents like those above are known and therefore serve to show that associated substances are to a marked degree chemically active. Further, just as with molecular association, so also the formation of additive compounds occurs least readily with ortho-substituted benzene derivatives and much more readily with meta- and para-derivatives.[268] Again, the organic oxygen compounds which form the most stable compounds with salts are those in which the oxygen is attached to hydrogen, whilst, in general, the organic substances either of high dielectric constant or high association factor form the most stable addition compounds with magnesium bromide or iodide. Menschutkin [269] found the order of decreasing stability of these addition compounds as below :—

Urea	Ethyl alcohol	Ethyl orthoformate
Water	Acetonitrile	Benzaldehyde
Aniline	Acetic anhydride	Methyl acetate
Acetamide	Acetic acid	Acetal
Ethyl urethane	Propionic acid	Acetyl chloride
Formic acid	Ethyl acetate	Ether
Methyl alcohol	Acetone	Anisol

Although it is clear that associated substances are so often chemically active, it is not necessary, however, that either or both constituents of an additive compound shall be associated. In the above list, the substances in the last column are unassociated, and the order of stability in the other two columns is not the order of the degree of association. More convincing is the fact that many additive compounds are formed from unassociated constituents. Among organic substances, examples of this type are the compounds of trinitrobenzene with the ortho-, meta- and para-toluidines, the benzidines, xylidenes and tolidenes;[270] of napthalene, phenanthrene and fluorene with di- and

trinitrobenzenes and trinitrotoluene ;[271] of ethyl bromide with bromine,[248] benzyl chloride with methylaniline,[248] ethyl acetate with bromine [272] and many others.

Then, on the other hand, substances known to be associated, such as formamide and water, may be mixed without combination occurring.[273] It has usually been supposed that what happens in such cases is a dissociative action, that the forces which cause the molecules of any pure substance to form aggregates exert such an attraction on a different aggregated molecule as to cause disruption of each. It has been pointed out in an earlier chapter (p. 48) that such an idea is not generally true. Some very surprising results obtained by English and the writer [274] indicate how very wide of the mark such an idea may be, since, instead of bringing about dissociation, an increase in the degree of association results, at any rate when salts are mixed. Thus, triethylammonium chloride and triethylammonium bromide are each strongly associated in bromoform. When introduced together into the same solvent, the depression of freezing-point observed ought to be greater than the value calculated from the independent depressions if mutual dissociation occurred. Instead, the observed was always less than the calculated depression by an amount which reached a maximum at a certain concentration and then declined, as will be seen from the following table. Δ_o and Δ_c represent the observed and calculated depressions. The concentrations of the substances are expressed as grams per 100 of solvent, the chloride being dissolved first and then successive additions of bromide made.

	Concn.	D_o.	$D_c - D_o$.
1. Chloride	1·692	0·775	—
Bromide	0·2601	0·812	0·118
	0·6368	0·836	0·224
	1·652	0·958	0·312
2. Chloride	1·728	0·786	—
Bromide	2·561	1·163	0·275
	3·469	1·365	0·224
	5·044	1·818	0·010

The extent of the deviation depends on the solvent. In water it is considerably less, but no enhanced dissociation is found to occur.

Evidently associated molecules are centres of very considerable activity. In some cases chemical combination occurs when two associated substances are brought together, in others

(salts in particular) there appears to be repulsion rather than attraction between the molecules. Unsaturation, as measured by the power of chemical action, cannot satisfactorily be accounted the cause of association. The mere presence of trivalent nitrogen, or of elements like chlorine, bromine and iodine, oxygen and sulphur does not bring about molecular association. It is only when these elements are present in one of the electronegative groups mentioned in chaps. III. and VII. that association occurs. Theories of valency which have up to the present been applied to explain the occurrence of molecular association are all unsatisfactory because they are founded on the supposed behaviour of unsaturated elements.[77]

A study of the factors which influence both molecular association and molecular compound formation also reveals some similarities and some differences between the two phenomena. The effect of rise of temperature is in both cases to cause increased dissociation. Pressure or concentration likewise affects each similarly; thus, the degree of combination between phenol and α-naphthylamine in benzene solution[274] increases as the concentration becomes greater, whilst, as already shown (chap. III.) increase of concentration raises the degree of molecular aggregation. The effect of the solvent, however, appears to be different in the two phenomena. On molecular association, the dielectric character of the solvent exerts a dominant influence. The influence of the solvent on the combination between triethylamine and ethyl iodide appears to have no reference to its dielectric constant.[275]

All these facts taken together have led to the suggestion,[77],[274] that the forces causing molecular association are either different in origin from those which bring about chemical action; or, if of the same origin, then they act differently. Possibly in molecular association we have to do with electrical as distinct from chemical forces.

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APPENDIX.

This appendix, as previously mentioned in the text, contains a summary up to date of the various investigations of molecular complexity of dissolved substances, with the concentrations calculated in most cases in terms of grams of substance per 100 grams of solvent. In a few cases the concentration is expressed in terms of milligram molecules per 100 c.c. of solvent (N), or, as milligram molecules per 100 grams of solvent (*n*). Where the molecular weights were not recorded by the investigator, they have been calculated using the depression or elevation constant quoted in the paper.

Some of the substances quoted have been investigated, in the same solvent, by a number of observers. In such cases all references are given but only one set of figures is recorded, namely, that drawn from the first reference quoted.

The nomenclature adopted is not always that in common use in current English chemical literature, but is, with slight variation only, that given by the investigator of the substance.

It is not easy to define clearly where molecular association exists. The majority of the substances in the table are distinctly associated. Other results are quoted, however, to illustrate the effect either of substitution on the degree of complexity, or of the influence of the solvent. At the end of the appendix a list of substances, or classes of substances, which may be considered as normal, is given.

High molecular weight results are also obtained when solvent and solute form solid solutions and association of the solute does not occur. Such cases have been excluded from the tables, but aniline, pyrrole, pyridine (pp. 143, 144), and cyclohexanone and its derivatives (p. 146) in cyclohexane or dicyclohexyl are doubtful. Probably association has little, if anything, to do with the abnormal numbers found.

A considerable number of freezing-point and boiling-point measurements on aqueous solutions, mainly of inorganic substances, are given in Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, to which source the reader is referred.

ALCOHOLS.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Methyl alcohol (carbinol)	CH_3OH	32	Benzene [1, 2]	0·32-7·29	43-144
			Nitrobenzene [2]	?	63·7
			Water [141]	3·35-10·92	32·0-31·6
Trimethyl carbinol	$(CH_3)_3C.OH$	74	Benzene [3, 1, 6]	0·220-10·43	73-166
			Bromoform [4]	0·1785-8·351	80·4-214·9
			Nitrobenzene [5]	0·5325-11·943	79·8-178·3
Dimethyl ethyl carbinol	$(CH_3)_2 \diagdown C.OH \diagup C_2H_5$	88	Benzene [3]	0·217-11·19	89-165
Dimethyl allyl carbinol	$(CH_3)_2 \diagdown C.OH \diagup (C_3H_5)$	100	Benzene [3]	0·243-10·07	93-144
Methyl diethyl carbinol	$CH_3 \diagdown C.OH \diagup (C_2H_5)_2$	102	Benzene [3]	0·248-10·14	102-143
Methyl ethyl allyl carbinol	$(CH_3)(C_2H_5)(C_3H_5)C.OH$	114	Benzene [3]	0·257-12·16	116-158
Methyl propyl allyl carbinol	$(CH_3)(C_3H_7)(C_3H_5)C.OH$	128	Benzene [3]	0·248-11·65	118-169
Methyl dipropyl carbinol	$(CH_3)(C_3H_7)_2C.OH$	130	Benzene [3]	0·263-10·95	121-151
Methyl *n*-butyl allyl carbinol	$(CH_3)(C_4H_9)(C_3H_5)C.OH$	142	Benzene [3]	0·325-12·44	131-185
Methyl allyl *tertiary*-butyl carbinol	$(CH_3)(C_3H_5)C.C(CH_3)_3 \diagdown OH$	142	Benzene [3]	0·266-12·79	129-160
Methyl hexylcarbinol	$(CH_3)(C_6H_{13})CHOH$	130	Benzene [3]	0·273-17·18	122-272
Triethyl carbinol	$(C_2H_5)_3C.OH$	116	Benzene [3]	0·346-8·586	108-134
Diethyl propyl carbinol	$(C_2H_5)_2(C_3H_7)C.OH$	130	Benzene [3]	1·84-11·73	144-166
Diethyl allyl carbinol	$(C_2H_5)_2(C_3H_5)C.OH$	128	Benzene [3]	0·267-12·34	111-161
Ethyl dipropyl carbinol	$(C_2H_5)(C_3H_7)_2C.OH$	144	Benzene [3]	0·257-12·48	132-178
Allyl dipropyl carbinol	$(C_3H_5)(C_3H_7)_2.C.OH$	156	Benzene [3]	0·259-13·55	130-194
Triphenyl carbinol	$(C_6H_5)_3.C.OH$	260	Benzene [3]	0·420-8·021	238-265

Diphenyl carbinol (Benzhydrol)	$(C_6H_5)_2$ CHOH	184
Ethyl alcohol	C_2H_5OH	46
n-Propyl alcohol	C_3H_7OH	60
iso-Propyl alcohol	C_3H_7OH	60
n-Butyl alcohol	C_4H_9OH	74
iso-Butyl alcohol		74
secy.-Butyl alcohol	C_4H_9OH	74
Amyl alcohol	$C_5H_{11}OH$	88
iso-Amyl alcohol	$C_5H_{11}OH$	88
Amyl mercaptan	$C_5H_{11}SH$	104
n-Heptyl alcohol	$CH_3(CH_2)_5CH_2OH$	116
n-Octyl alcohol	$CH_3(CH_2)_6CH_2OH$	130
Capryl alcohol	$C_6H_{13}OH$	102
Cetyl alcohol	$C_{16}H_{33}OH$	242
Allyl alcohol	$CH_2 : CH.CH_2OH$	58
Linalool	$(CH_3)_2C : CH \quad CH_3$ $\quad\quad\quad

Substan.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Monochlorhydrin	$CH_2Cl.CHOH : CH_2OH$	110·5	Benzene [6]	1·3-6·6	85·57-130·0
Dichlorhydrin	$CH_2Cl.CHOH.CH_2Cl$	129	Benzene [6]	2·1-10·5	102·8-136·7
Epichlorhydrin	C_3H_5OCl	92·5	Benzene [6]	1·9-8·0	95·57-103·0
Benzyl alcohol	$C_6H_5CH_2OH$	108	Naphthalene [1]	0·99-7·35	106-139
			Benzene [1, 6]	0·92-20·70	118-271
			Nitrobenzene [5]	0·620-59·299	112-342
			Bromoform [4]	0·4441-12·5514	112·2-262·2
o-Nitrobenzyl alcohol	$C_6H_4(NO_2)CH_2OH$	153	Naphthalene [11]	1·00-9·06	143-182
p-Nitrobenzyl alcohol	$C_6H_4(NO_2)CH_2OH$	153	Naphthalene [11]	0·91-8·34	170-189
Benzoin	$C_6H_5.CHOH.CO.C_6H_5$	212	Benzene [1]	0·15-0·54	211-230
Cinnamic alcohol	$C_6H_5.CH : CH.CH_2OH$	134	Benzene [3]	0·292-16·46	130-323
Borneol	$C_{10}H_{18}O$	154	Benzene [8, 14]	0·430-16·28	150-232
			Acetic acid [8]	0·959-27·62	155-199
			Ethyl alcohol [14]	1·61-15·06	154-179
			Ether [15]	1·93-4·17	139-156
			Cyclohexane [125]	0·22-4·75	179·0-340·6
Menthol	$C_{10}H_{20}O$	156	Benzene [13, 16]	0·60-23·93	151-322
			p-Dichlorobenzene [13]	0·47-9·18	176-192
			Ether [15]	1·30-3·31	140-161
			Cyclohexane [125]	0·34-6·46	193·4-403·7

PHENOLS.

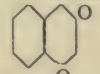
Substance	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Phenol	C_6H_5OH	94	Ethylene bromide [7]	0·252-4·176	95·9-135·7
			Methyl succinate [7]	0·378-4·123	93·2-101·2
			Water [17, 10]	1·115-5·156	96·5-106·9
			Benzene [8, 1, 10, 2]	0·338-36·56	144-252
			Acetic acid [8]	1·001-18·22	100-107
			Diphenylmethane [29]	1·178-7·598	106·8-129·6
			Ether [18]	4·641	96·5
			Naphthalene [19, 20]	0·39-5·34	98·9-113
			Cyclohexane [21]	1·75-3·12	240-316

o-Nitrophenol	$C_6H_4(NO_2)OH$	139
m-Nitrophenol	$C_6H_4(NO_2)(OH)$	139
p-Nitrophenol	$C_6H_4(OH)NO_2$	139
o·o-Dibromo *p*-nitrophenol	$C_6H_2(Br)_2(NO_2)OH$	297
2·4-Dinitrophenol	$C_6H_3(OH)(NO_2)_2$	184
α-Dinitropheno	$C_6H_3(OH)(NO_2)_2$	184
2·4·6-Trinitrophenol	$C_6H_2(OH)(NO_2)_3$	229

Dicyclohexyl [124]	1·32	238·9
p-Bromotoluene [9]	2·179-42·877	117·6-349·6
Bromoform [4]	0·1987-9·10	98·7-252·6
Nitrobenzene [5]	1·072-17·25	85-127
Benzene [1]	0·25-5·39	123-136
Nitrobenzene [22]	0·93-8·89	138-151
Naphthalene [22, 23, 19]	0·98-13·86	144-153
m-Dinitrobenzene [22]	0·97-5·64	132-143
p-Bromobenzene [22]	0·72-5·99	145-157
Benzil [22]	0·84-5·66	132-145
Naphthalene [19, 23]	0·82-12·08	147-194
p-Dibromobenzene [22]	1·04-5·34	172-253
p-Chlorobromobenzene [22]	0·93-3·88	171-219
p-Dichlorobenzene [22]	0·51-3·11	147-201
Benzene [17, 1]	3·052-7·134	151-194
Water [17]	2·203-5·641	156-196
Nitrobenzene [22]	0·88-8·48	270-253
m-Dinitrobenzene [22]	0·93-6·86	135-158
p-Nitrotoluene [22]	0·92-7·66	161-170
2·4-Dinitrotoluene [22]	1·04-7·28	138-154
2·4·6-Trinitrophenol [22]	0·86-6·15	158-182
p-Chloronitrobenzene [22]	0·88-6·75	173-213
p-Dichlorobenzene [22]	0·40-2·13	156-227
p-Chlorobromobenzene [22]	0·50-2·45	168-252
p-Dibromobenzene [22]	0·88-6·59	172-353
Naphthalene [19, 22, 23]	0·64-10·53	133-210
Dimethyloxalate [24]	0·95-8·80	157-152
p-Azoxyanisole [24]	0·411-1·439	136-138
Naphthalene [19]	0·67-12·94	300-310
Nitrogen peroxide [26]	0·46-1·75	186-177
Naphthalene [19, 23]	0·33-6·54	170-185
Benzene [1]	0·38-2·78	193-188
Nitrogen peroxide [26, 134]	2·29-10·50	219-257
Chloroform [27]	1·004-6·673	212-252
Acetic acid [28]	0·865	228
Benzene [12, 27, 1]	0·34-2·81	210-238
Naphthalene [19]	0·60-5·24	220-231

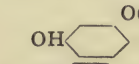
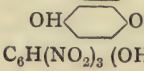
Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
o-Cyanophenol	C_6H_4 (OH) CN	119	*p*-Dibromobenzene [22]	1·03-5·11	152-310
			p-Chlorobromobenzene [22]	1·07-4·61	190-379
			p-Dichlorobenzene [22]	1·97-8·72	208-525
			p-Bromotoluene [13]	0·37-1·99	179-314
			p-Iodotoluene [13]	0·47-1·59	206-317
			p-Nitrotoluene [13]	0·88-5·95	144-169
			p-Toluidine [13]	0·86-6·78	116-117
			Methyl *p*-toluate [13]	1·84-7·77	120-136
			Methyloxalate [24]	0·99-9·09	119-138
			Naphthalene [22]	2·19-18·25	149-342
m-Cyanophenol	C_6H_4 (OH) CN	119	*p*-Dibromobenzene [22]	1·06-5·08	165-321
			p-Chlorobromobenzene [22]	0·74-3·06	197-233
			p-Dichlorobenzene [22]	1·56-7·63	194-421
			p-Xylene [13]	0·40-1·90	143-190
			p-Bromotoluene [13]	0·23-1·97	173-264
			p-Iodotoluene [13]	0·48-1·70	194-308
			p-Nitrotoluene [13]	1·09-6·13	142-163
			Methyl *p*-toluate [13]	1·58-10·98	133-138
p-Cyanophenol	C_6H_4 (OH) CN	119	*p*-Dibromobenzene [22]	0·72-3·96	176-349
			p-Chlorobromobenzene [22]	0·76-3·85	175-427
			p-Dichlorobenzene [22]	0·74-2·28	195-305
			p-Nitrotoluene [13]	1·14-6·25	174-187
			p Toluidine [13]	1·17-8·81	110-114
			Methyl *p*-toluate [13]	2·27-10·92	123-138
			Naphthalene [25]	0·99-10·00	131-248
			Methyloxalate [24]	0·98-8·87	127-139
3-Nitro *p*-cyanopheno	C_6H_3 (OH) (CN) NO_2	164	Naphthalene [25]	1·05-9·51	163-171
3·5-Dichloro *p*-cyanophenol	C_6H_2 (OH) (CN) Cl_2	188	Naphthalene [25]	0·97-6·12	188-208
3-Bromo *p*-cyanophenol	C_6H_3 (OH) (CN) Br	198	Naphthalene [25]	1·02-7·80	201-233
3·5-Dibromo *p*-cyanophenol	C_6H_2 (OH) (CN) Br_2	277	Naphthalene [25]	1·34-8·23	277-293
3·5-Diiodo *p*-cyanophenol	C_6H_2 (OH) (CN) I_2	371	Naphthalene [25]	1·28-6·14	366-370
o-Chlorophenol	C_6H_4 (Cl) OH	128·5	Naphthalene [19]	1·29-8·74	123-137
p-Chlorophenol	C_6H_4 (Cl) OH	128·5	Naphthalene [19, 20]	0·45-10·21	137-157

o-Bromophenol	C_6H_4 (OH) Br	173	Naphthalene [19, 20]	1·54-9·66	174-186
			Benzene [12]	0·58-9·46	161-187
p-Bromophenol	C_6H_4 (OH) Br	173	Naphthalene [19]	0·47-10·27	153-196
Tribromophenol	C_6H_2 $(Br)_3$ OH	331	Benzene [1]	2·5-3·99	340-327
			Cyclohexane [125]	0·46-2·09	313·8-322·8
p-Iodophenol	C_6H_4 (OH)I	220	Naphthalene [19]	1·48-6·84	233-241
Benzeneazophenol	$C_6H_5N : NC_6H_4OH$	198	Naphthalene [20]	0·97-10·34	202-242
			Benzene [1]	0·37	216
o-Tolueneazophenol	C_6H_4 (CH_3) N : N.C_6H_4OH	212	Naphthalene [20]	1·09-8·24	210-234
o-Nitrobenzeneazophenol	C_6H_4 (NO_2).N : N.C_6H_4OH	243	Naphthalene [20]	1·23-10·11	245-305
m-Nitrobenzeneazophenol	C_6H_4 (NO_2).N : N.C_6H_4OH	243	Naphthalene [20]	1·08-9·57	247-288
p-Nitrobenzeneazophenol	C_6H_4 (NO_2).N : N.C_6H_4OH	243	Naphthalene [20]	1·06-3·13	241-257
o-Methoxybenzeneazophenol	C_6H_4 (OCH_3).N : N.C_6H_4.OH	228	Naphthalene [20]	1·03-7·96	229-306
p-Methoxybenzeneazophenol	C_6H_4 (OCH_3).N : N.C_6H_4.OH	228	Naphthalene [20]	1·08-9·41	225-270
o-Ethoxybenzeneazophenol	C_6H_4 (OC_2H_5).N : N.C_6H_4OH	242	Naphthalene [20]	1·20-10·21	244-332
m-Ethoxybenzeneazophenol	C_6H_4 (OC_2H_5).N : N.C_6H_4OH	242	Naphthalene [20]	1·21-9·85	236-278
p-Ethoxybenzeneazophenol	C_6H_4 (OC_2H_5).N : N.C_6H_4OH	242	Naphthalene [20]	1·12-6·90	234-266
o-Cresol	C_6H_4 (CH_3) OH	108	Naphthalene [19, 23]	1·15-8·75	115-131
			Cyclohexane [125]	0·95-7·19	134·2-309·1
p-Cresol	C_6H_4 (CH_3) OH	108	Benzene [1]	1·15-18·38	107-208
			Naphthalene [19, 23]	0·36-10·14	112-142
			p-Bromotoluene [9]	0·411-38·96	113·5-359·8
			Cyclohexane [125]	0·63-9·62	156·3-562·6
			Nitrobenzene [5]	0·5863-23·43	134-161
			Stearic acid [29]	3·520-24·16	117·7-138·5
			Cyclohexane [125]	0·73-13·06	166·5-669·8
p-Bromocresol	C_6H_3 (OH) (CH_3) Br	187	Benzene [30]	2·192-11·535	186-208
p-Bromo-*o*-bromocresol	C_6H_3 (OH) (CH_2Br) Br	266	Benzene [30]	1·793-8·937	275-285
2·4-Dibromo-*o*-cresol	C_6H_2 (OH) (CH_3) Br_2	266	Benzene [30]	2·148-10·109	250-272
2·4-Dibromo-*o*-Bromocresol	C_6H_2 (OH) $(CH_2Br).Br_2$	345	Benzene [30]	1·840-8·887	326-347
p-Nitro-*o*-chlorocresol	C_6H_3 (OH) (NO_2) CH_2Cl	187·5	*p*-Dibromobenzene [30]	0·792-5·011	202-316
o-Nitro-*p*-chlorocresol	C_6H_3 (OH) (NO_2) CH_2Cl	187·5	*p*-Dibromobenzene [30]	0·888-4·734	184-203
p-Nitro-*o*-bromocresol	C_6H_3 (OH) (NO_2) CH_2Br	232	*p*-Dibromobenzene [30]	1·584-4·724	284-354
o-Nitro-*p*-bromocresol	C_6H_3 (OH) (NO_2) CH_2Br	232	*p*-Dibromobenzene [30]	1·615-5·676	228-240
p-Carbethoxy-*o*-cresol	C_6H_3 (OH) (CH_3) $CO_2C_2H_5$	180	*p*-Dibromobenzene [30]	1·253-4·697	239-307
p-Carbethoxy-*o*-chlorocresol	C_6H_3 (OH) (CH_2Cl) $(CO_2C_2H_5)$	214·5	*p*-Dibromobenzene [30]	2·133-10·123	301-478
p-Carbethoxy-*o*-bromocresol	C_6H_3 (OH) (CH_2Br) $(CO_2C_2H_5)$	259	*p*-Dibromobenzene [30]	1·172-6·194	328-457

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
o-Bromo-*p*-nitro-*o*-cresol	$C_6H_2(NO_2)(Br)(OH)(CH_3)$	232	*p*-Dibromobenzene [30]	1·840-6·870	249-267
o-Bromo-*p*-nitro-*o*-bromocresol	$C_6H_2(NO_2)(Br)(OH)CH_2Br$	311	*p*-Dibromobenzene [30]	1·923-6·165	318-352
p-Nitro-*o*-acetoxycresol	$C_6H_3(NO_2)(OH)CH_2.CO_2CH_3$	211	*p*-Dibromobenzene [30]	0·693-4·972	200-273
m-Nitro-*p*-cresol	$C_6H_3(CH_3)(NO_2)OH$	153	Naphthalene [19]	0·44-8·20	157-159
o-Nitro-*p*-cresol	$C_6H_3(CH_3)(NO_2)OH$	153	*p*-Dibromobenzene [30]	0·937-2·768	159-173
p-Nitro-*o*-cresol	$C_6H_3(CH_3)(NO_2)OH$	153	*p*-Dibromobenzene [30]	1·082-6·224	184-302
m-Dinitro-*p*-cresol	$C_6H_2(CH_3)(NO_2)_2OH$	198	Naphthalene [19]	1·44-7·66	201-205
p-Thiocresol	$C_6H_4(CH_3)SH$	124	Naphthalene [11]	1·27-9·18	131-137
o-Methoxy-*m*-thiocresol	$C_6H_3(CH_3)(OCH_3)SH$	154	Naphthalene [11]	0·85-9·98	170-177
o-Xylenol	$C_6H_3(CH_3)_2OH$	122	Naphthalene [19]	0·65-10·12	126-157
m-Xylenol	$C_6H_3(CH_3)_2OH$	122	Naphthalene [19]	0·39-6·35	129-137
p-Xylenol	$C_6H_3(CH_3)_2OH$	122	Naphthalene [19]	0·55-13·04	117-145
asy-*m*-Xylenol	$C_6H_3(CH_3)_2OH$	122	Naphthalene [20]	1·12-8·93	123-141
α-Naphthol	$C_{10}H_8O$	144	*p*-Dibromobenzene [31]	1·51-6·38	149-174
			Benzene [1]	0·26-4·99	127-147
β-Naphthol	$C_{10}H_8O$	144	*p*-Dibromobenzene [31]	0·60-5·84	158-184
			Pyridine [32]	0·93-9·68	158-144
			Benzene [33, 1]	2·118-3·584	141-135
			Stearic acid [29]	1·734-7·886	165·3-168·8
p-Nitro-*α*-naphthol	$C_{10}H_6(NO_2)OH$	189	*p*-Dibromobenzene [31]	0·60-2·32	255-292
β-Nitro-*α*-naphthol	$C_{10}H_6(NO_2)OH$	189	*p*-Dibromobenzene [31]	0·32-3·62	193-218
α-Nitro-*β*-naphthol	$C_{10}H_6(NO_2)OH$	189	*p*-Dibromobenzene [31]	0·55-2·50	167-194
Nitroso-naphthol		173	Acetone [34]	2·46-3·74	177·3-201·6
			Ethyl alcohol [34]	2·56-4·48	181·2-209·7
			Acetone [34]	3·20-5·93	174·7-176·4
			Ethyl alcohol [34]	2·5-3·8	176·3-177·7
			Acetone [34]	1·94-3·20	174·0-175·6
			Ethyl alcohol [34]	1·94-3·41	176·2-175·6

Decahydronaphthol	$C_{10}H_{18}O$	154	Naphthol [128]	0·47-2·94	148-141
Pseudo-cumenol	$C_6H_2(CH_3)_3OH$	136	Naphthalene [20]	1·58-9·85	138-156
Guaiacol	$(CH_3)_3C_6H_2OH$	124	Naphthalene [19, 24]	0·70-9·07	114-135
Thymol	$(CH_3)_2.CH.C_6H_3(CH_3)OH$	150	Ethyl ether [14, 15]	2·35	145
			Benzene [1]	1·28-17·71	146-184
			Naphthalene [19]	0·42-8·54	147-159
			p-Bromotoluene [9]	0·369-13·057	132·8-171·6
			Bromoform [4]	0·1913-10·16	121·7-193·9
			Nitrobenzene [5]	0·4628-30·18	124-187
			Cyclohexane [125]	0·37-14·94	140·1-395·8
Eugenol	$C_6H_3(C_3H_5)(OCH_3)OH$	164	Diphenylmethane [29]	0·995-5·097	175 193·5

DIHYDROXYPHENOLS.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Catechol	$C_6H_4(OH)_2$	110	Water [17]	3·283-5·218	123·9-127·4
			Benzene [17, 1]	3·085-6·639	119-137
			Ether [14]	2·34	106
			Naphthalene [19, 24]	0·46-6·42	116-144
Resorcinol	$C_6H_4(OH)_2$	110	Water [17]	3·286-3·997	119·7-119·9
			Benzene [17]	1·751-3·703	114-136
			Pyridine [32]	0·57-4·17	124-105
			Ether [37, 36, 33]	2·06-8·99	112-127
			Ethyl alcohol [36, 37, 38]	1·99-5·05	110·5-113·0
			Naphthalene [19, 24]	0·44-2·88	112-139
			Acetone [38]	5·81	98
Quinol	$C_6H_4(OH)_2$	110	Ether [18]	1·913	113
			Naphthalene [19]	0·36	90
Resorcinol methyl ether		124	Naphthalene [24]	0·55-6·78	125-152
Hydroquinone methyl ether		124	Naphthalene [24]	1·08-3·09	127-144
Styphnic acid	$C_6H(NO_2)_3(OH)_2$	245	Naphthalene [19]	0·695	259

TRIHYDRIC PHENOLS.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Pyrogallol	$C_6H_3(OH)_3$	126	Naphthalene [19]	0·31-1·04	128-143
			Ethyl ether [14]	1·85	130
			Water [17]	5·540-12·79	139-142
Phloroglucinol	$C_6H_3(OH)_3$	126	Water [17]	4·635-10·98	168-156

ACIDS.

Sub tance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Formic acid	H.COOH	46	Nitrobenzene [5]	0·849-34·96	77-301
			Benzene [2]	?	99·1
			Water [141]	4·708-27·28	46·7-51·1
Acetic acid	CH_3.COOH	60	Nitrogen peroxide [134, 26]	0·28-2·25	194-178
			Carbonyl chloride [39]	0·46-1·44	119-128
			Cyclohexane [125]	0·86-3·49	121·7-149·0
			Dicyclohexyl [124]	0·75-3·03	133·2-166·6
			Sulphur dioxide [39]	0·49-2·55	76·2-94·1
			Ethylene bromide [7, 2]	0·173-4·921	99·5-149·4
			Methyl succinate [7]	0·421-3·334	60·6-77·4
			Veratrol [7]	0·389-4·954	63·8-84·1
			Benzene [10, 8, 2]	0·345-14·08	100·8-123·6
			p-Bromotoluene [9]	0·3395-34·74	82·0-250·0
			Bromoform [4]	0·2240-7·49	91·3-174·6
			Nitrobenzene [5, 2]	0·346-18·10	85-157
			Water [149]	0·5709-6·956	58·8-62·0
			Phosphorus oxychloride [126]	2·83-14·82	94·9-124·4
Chloroacetic acid	CH_2Cl.COOH	94·5	Benzene [1]	2·50	182
			Phosphorous oxychloride [126]	0·90-7·00	94·7-112·3
Bromoacetic acid	CH_2Br.COOH	139	Benzene [1]	0·98-9·64	246-278
Thioacetic acid	CH_3COSH	76	Naphthalene [11]	1·05-4·77	80-99
Phenylacetic acid	$C_6H_5CH_2$.COOH	136	Water [17]	5·038-9·124	183-225
			Benzene [17, 1]	3·556-8·740	209-231

Phenoxyacetic acid	$(C_6H_5O)\,CH_2.COOH$	152	Naphthalene [20]	0·62-9·15	204-254
Dichloroacetic acid	$CHCl_2.COOH$	128·9	Ethylene bromide [14]	0·57-4·93	168-210
Trichloroacetic acid	$CCl_3.COOH$	163·5	Phosphorus oxychloride [126]	0·69-8·07	115·9-117·3
			Formic Acid [41]	1·367-2·876	158·6-139·0
Tribromoacetic acid	$CBr_3.COOH$	297	Phosphorus oxychloride [126]	0·94-10·88	142·9-134·6
			Nitrogen peroxide [134]	1·00-1·77	258·3-277·3
			Benzene [1]	1·00-5·56	312-467
Propionic acid	$C_2H_5.COOH$	74	Nitrogen peroxide [26]	0·93-3·80	552-606
			Formamide [42]	3·359-4·748	242·9-237·4
			Water [17]	0·823-15·47	66·8-84·8
Phenylpropionic acid	$C_6H_5.CH_2.CH_2.COOH$	150	Benzene [17, 1]	1·320-12·85	139·8-151·9
			Phosphorus oxychloride [126]	0·81-7·09	97·1-128·1
			Diphenyl [29]	2·509	260·8
			p-Cresol [29]	2·605-11·40	159·2-164·5
			Anethol [29]	1·710-17·46	258·1-236·2
			Azobenzene [29]	0·915-8·648	244·2-258·3
Butyric acid	$C_3H_7.COOH$	88	Phosphorus oxychloride [126]	0·64-4·94	108·3-136·8
			Water [17]	1·847-9·605	81·7-99·1
			Nitrogen peroxide [134]	0·507-1·22	208-217
			Benzene [17]	0·951-11·20	157·0-174·6
			Bromoform [4]	0·6924-11·2364	143·7-239·6
			Nitrobenzene [5]	0·3336-37·3474	104-259
Trichlorobutyric acid	$C_3H_4Cl_3.COOH$	191·5	Nitrogen peroxide [26]	0·85-6·97	233-281
			Benzene [1]	9·98	333
Valeric acid	$CH_3(CH_2)_3COOH$	102	Nitrobenzene [5, 2]	0·3750-41·49	143-351
			Benzene [2]	?	188·2
Isonitrosovaleric acid	$CH_3.CH(NO)(CH_2)_2\,COOH$	131	Phenol [43]	1·575-9·979	139-203·8
Caproic acid	$C_5H_{11}.COOH$	116	Benzene [1]	1·05-16·29	194-221
Caprylic acid	$C_7H_{15}.COOH$	144	Benzene [1]	1·99-11·39	247-255
Lauric acid	$C_{11}H_{23}.COOH$	200	Benzene [1]	0·72-16·30	320-370
Chlorocrotonic acid	$CH_2Cl.CH:CH.COOH$	120·5	Benzene [1]	1·18-3·28	164-227
Carvocrotonic acid		190	Benzene [1]	1·04	308
Cinnamic acid	$C_6H_5.CH:CH.COOH$	148	Benzene [1]	1·45	258
			Nitrobenzene [44, 5]	0·44-1·20	265-307
			Diphenylmethane [29]	0·389-1·559	331·6-382·9
Phenylcinnamic acid	$C_6H_5\,CH:C.(C_6H_5).COOH$	224	Phenol [29]	7·355-9·638	194·8-196·1
			Benzene [1]	0·95	348

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Oxalic acid	COOH.COOH	90	Water [17]	4·700-9·677	72·1-74·7
Malonic acid	$CH_2(COOH)_2$	104	Ethyl Ether [14]	2·08	110
Succinic acid	$(CH_2.COOH)_2$	118	Ethyl alcohol [14]	2·12-5·78	123-113
			Water [17]	4·487-7·591	123-118·9
			Pyridine [32]	1·18-8·40	127-113
Benzoic acid	$C_6H_5.COOH$	122	Nitrogen peroxide [26]	2·45-9·26	209-228
			Carbon disulphide [14, 46]	1·87-9·09	237-273
			p-Dibromobenzene [13]	0·47-4·14	196-255
			m-Dinitrobenzene [13]	1·15-6·17	148-190
			Methyl *p*-toluate [13]	0·50-8·68	163-170
			Carbonyl chloride [39]	0·59-1·61	244-267
			Sulphur dioxide [39]	1·47-7·85	214-237
			Nitrobenzene [44, 2]	0·305-2·01	260-273
			Water [17]	6·088-7·288	235-258
			Benzene [14, 8, 38, 2]	2·91-10·75	210-250
			Acetic acid [8, 14]	0·857-24·92	123-146
			Ether [14, 18]	1·26-22·10	120-148
			Phenol [47, 29]	0·57-5·08	126-138
			Chloroform [14, 38, 48]	0·85-8·61	199-226
			Ethyl alcohol [14, 38, 48]	1·98-4·42	115-124
			Ethyl acetate [14]	0·79-18·55	121-144
			Naphthalene [20]	1·19-9·65	194-232
			Phosphorus oxychloride [126]	0·73-1·79	139·0-154·8
			Acetone [38]	8·58-4·97	115
			p-Toluidine [29]	2·314 9·139	158·3-139·8
			Cyclohexane [125]	0·45-0·55	227·6-231·1
o-Chlorobenzoic acid	$C_6H_4Cl.COOH$	156·5	Benzene [1]	0·58	258
			Naphthalene [20]	0·52-5·62	199-261
m-Chlorobenzoic acid	$C_6H_4Cl.COOH$		Naphthalene [20]	0·58-6·94	212-280
o-Bromobenzoic acid	$C_6H_4Br.COOH$	201	Naphthalene [20]	0·57-9·13	269-340
			Benzene [45]	2·47-19·4	307-364
m-Bromobenzoic acid	$C_6H_4Br.COOH$	201	Bromine [49]	0·29-0·81	290-301
			Naphthalene [20]	0·59-8·89	287-367
p-Bromobenzoic acid	$C_6H_4Br.COOH$		Naphthalene [20]	0·43-0·73	283-313

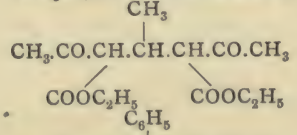
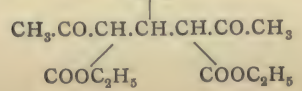
o-Iodobenzoic acid	$C_6H_4I.COOH$	248	Naphthalene [20]	0·59-9·00	320-417
Anthranilic acid	$C_6H_4(NH_2).COOH$	137	Benzene [1]	0·51	210
			Naphthalene [20]	0·64-5·77	201-249
p-Amidobenzoic acid	$C_6H_4(NH_2).COOH$	137	Naphthalene [20]	0·56	211
o-Nitrobenzoic acid	$C_6H_4(NO_2).COOH$	167	Naphthalene [20]	0·28-8·86	214-310
			Phosphorus oxychloride [126]	0·45-1·49	145·8-121·0
m-Nitrobenzoic acid	$C_6H_4(NO_2).COOH$		Naphthalene [20]	0·34-8·69	239-306
			Benzene [1]	0·54	282
p-Nitrobenzoic acid	$C_6H_4(NO_2).COOH$		Naphthalene [20]	0·18	246
o-o-Dinitrobenzoic acid	$C_6H_3(NO_2)_2.COOH$	212	Naphthalene [20]	0·29-0·80	222-229
m-m-Dinitrobenzoic acid	$C_6H_3(NO_2)_2.COOH$		Naphthalene [20]	0·36	292
sym-Trinitrobenzoic acid	$C_6H_2(NO_2)_3.COOH$	257	Naphthalene [20]	0·39-1·50	277-301
o-Toluic acid	$C_6H_4(CH_3).COOH$	136	Naphthalene [20]	0·58-5·80	175-230
			Nitrogen peroxide [26]	0·44-8·19	200-242
m-Toluic acid	$C_6H_4(CH_3).COOH$	136	Naphthalene [20]	0·62-9·25	212-250
			Nitrogen peroxide [26]	0·52-2·67	198-229
p-Toluic acid	$C_6H_4(CH_3).COOH$	136	Naphthalene [20]	0·62-6·54	209-252
			Nitrogen peroxide [26]	1·01-1·86	194-197
Phthalic acid	$C_6H_4(COOH)_2$	166	Water [17]	5·857-9·069	129-136
			p-Toluidine [29]	2·966	419·1
α-Carboxypyrrolic acid	$C_4H_3NH.COOH$	111	Acetic acid [50]	0·383-3·755	92-107
Benzoic anhydride	$(C_6H_5CO)_2O$	226	Benzene [8, 14]	1·101-3·456	213-277
			Acetic acid [8]	1·399-54·45	219-338
Phthalic anhydride	$C_6H_4(CO)_2O$	148	Acetic acid	1·59	169
			p-Toluidine	2·497-4·344	192·6-187·4

HYDROXY ACIDS.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Tartaric acid	COOH.CHOH.CHOH.COOH	150	Pyridine [32]	1·81-12·10	160-165
			Ethyl alcohol [14, 33, 38]	1·67-21·46	157-147
Salicylic acid	$C_6H_4(OH).COOH$	138	Pyridine [32]	0·98-12·00	123-140
			Water [17]	3·966-7·436	177-238
			Chloroform [14, 38]	0·87-5·09	211-254

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
			Benzene [14, 1, 38]	0·75-5·61	165-234
			Ethyl alcohol [14, 53, 38, 54, 48]	1·37-17·29	129-143
			Ether [14, 53]	1·40-2·86	137-136
			Naphthalene [20]	0·52-8·19	179-258
			p-Toluidine [29]	2·966-12·05	207·0-159·2
m-Hydroxybenzoic acid	C_6H_4 (OH).COOH	138	Water [17]	4·864-7·986	157-175
			Naphthalene [20]	0·21	218
p-Hydroxybenzoic acid	C_6H_4 (OH).COOH	138	Water [17]	4·318-7·236	141-157
			p-Toluidine [29]	1·252-3·430	179·1 185·8
Mandelic acid	C_6H_5 CH (OH).COOH	152	Water [17]	5·137-6·908	155-159
			Benzene [17]	2·263-4·063	209-260
Protocatechuic acid	C_6H_3 $(OH)_2$ COOH	154	Water [17]	5·556-11·46	188-193

ESTERS.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Dimethyl oxal-acetate	$COOCH_3.CH_2.CO.COOCH_3$	160	Benzene [12]	1·11-5·49	153-197
Diethyl oxal-acetate	$COOC_2H_5.CH_2.CO.COOC_2H_5$	188	Benzene [1]	0·32-8·50	218-295
Ethyl formyl-propionate	$CHO.CH(CH_3)COOC_2H_5$	130	Benzene [1]	0·22-7·93	136-153
Ethyl β-amido-crotonate	$CH_3.C(NH_2):CH.COOC_2H_5$	129	Benzene [1]	0·71-12·05	117-152
Sodium ethylate	$NaOC_2H_5$	68	Ethyl alcohol [59]	0·946-3·403	81-58
Ethyl acetoacetate	$CH_3.CO.CH_2.COOC_2H_5$	130	Benzene [1]	0·32-8·77	115-134
			Cyclohexane [127]	0·76-5·58	139-201·0
Monosodium ethyl acetoacetate	$CH_3.C(ONa):CH.COOC_2H_5$	152	Alcohol [59]	1·237-4·423	167-179
Ethylidene diacetoacetate		286	Benzene [12]	0·43-2·86	274-310
Benzylidene diacetoacetate		348	Benzene [12]	0·46-1·17	384-394

Methyl lactate	$CH_3.CH(OH).COOCH_3$	104	Benzene [12]	0·70-9·28	98·9-162
Ethyl lactate	$CH_3.CH(OH).COOC_2H_5$	118	Benzene [12]	0·40-11·82	107-176
Ethyl malonate	$CH_2:(COOC_2H_5)_2$	160	Ethyl alcohol [59]	1·234-5·782	160-177
Monosodium ethyl malonate	$CHNa:(COOC_2H_5)_2$	182	Ethyl alcohol [59]	2·082-6·127	155-204
Dimethylmalate	$COOCH_3.CHOH.CH_2.COOCH_3$	162·1	Benzene [60] (cryos.)	1·50-8·08	172·4-243·2
			Benzene [60] (ebul.)	1·32-13·26	180·5-229·9
			Methyl alcohol [61, 60]	1·97-18·48	207·4-221·7
			Ethyl acetate [60]	1·55-16·32	190·8-172·2
			Acetone [60, 61]	2·95-20·45	207·7-168·6
			Chloroform [60]	0·80-16·49	162·5-174·6
Diethylmalate	$COOC_2H_5.CHOH.CH_2.COOC_2H_5$	190·1	Ethyl acetate [60]	3·03-12·62	217-199·5
			Chloroform [60]	2·06-9·23	204·7-195·9
			Methyl alcohol [60]	4·31-15·71	211·6-197·2
			Acetone [60]	4·51-18·20	226·9-190·1
			Benzene [60]	cryos. 2·10-12·70	207·8-274·1
				ebul. 4·99-15·84	231·0-250·9
Dimethyl acetyl malate	$CH(COCH_3)CH(OH)(COOCH_3)_2$	204	Acetone [60]	3·13-14·09	244·2-201·9
			Methyl alcohol [60]	4·14-23·10	280·7-245·9
			Ethyl acetate [60]	3·84-22·97	222·3-214·9
			Chloroform [60]	1·08-17·55	220·1-169·2
			Carbon disulphide [60]	1·26-16·99	270·4-474·7
			Benzene [60] (ebul.)	1·82-9·62	203·6-220·9
			Benzene [60] (cryos.)	1·91-9·00	201·4-215·7
Dimethyl tartrate	$(CHOH.COOCH_3)_2$	178	Benzene [45]	1·23-23·10	185-348
			Ethyl acetate [60]	1·38-6·29	232·5-219·3
			Chloroform [60]	2·12-9·14	266·0-244·8
			Methyl alcohol [60]	3·57-12·85	209·6-183·2
			Acetone [60]	5·48-12·64	212·7-194·5
			Benzene [60]	3·64-12·85	220·6-305·1
			Acetonitrile [60]	2·52-10·07	207·3-193·4
Diethyl tartrate	$(CHOH.COOC_2H_5)_2$	206	Ethylene bromide [62, 63]	0·791-9·365	228-354
			Water [64]	2·78-8·40	194·8-204·2
			Methyl alcohol [61, 60, 64]	1·80-14·36	171·8-196·2
			Ethyl alcohol [64]	4·54-10·58	205·1-226·6
			n-Propyl alcohol [64]	4·61-10·90	182·8-229·5
			Benzene [65] (cryos.)	0·386-7·895	210·0-344·2
			Benzene [65] (ebul.)	0·232-10·565	172·0-277·4

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
			p-Xylene [66]	0·296-16·75	205·5-539·4
			Acetone [60, 61]	3·81-17·32	259·5-209·9
			Ethyl acetate [60]	0·91-11·50	242·4-217·1
			Chloroform [60]	2·06-9·91	235·4-234·8
			Benzene [60] (ebul.)	5·07-16·92	274·3-318·5
			Benzene [60] (cryos.)	2·51-11·18	252·5-387·4
Di-*iso*butyl tartrate	$(CHOH.COOC_4H_9)_2$	262·2	Sulphur dioxide [66]	14·2	258
Ethyl diacetyl glycerate (active)	$COOC_2H_5.CH.(COOCH_3)$ / $CH_2.(COOCH_3)$	218	Benzene [67]	3·52-22·41	268·7-226·1
			Acetic acid [67]	1·01-19·19	135·7-193·6
Methyl salicylate	$C_6H_4(OH).COOCH_3$	152	2·4-Dinitrotoluene [22]	1·54-6·27	159-163
			2·4·6-Trinitrotoluene [22]	0·56-1·92	128-151
			p-Nitrotoluene [22]	0·95-1·97	156-157
			p-Chloronitrobenzene [22]	0·53-1·36	159-147
			Naphthalene [22, 19, 20, 23]	1·66-23·12	151-171
			p-Azoxyanisol [24]	0·625-1·755	142-149
			Nitrobenzene [22]	1·65-9·87	144-160
			p-Dibromobenzene [22]	1·01-5·34	145-156
			Benzil [22]	0·92-5·60	145-157
Methyl *m*-hydroxybenzoate	$C_6H_4(OH).COOCH_3$	152	*p*-Chlorobromobenzene [22]	0·97-4·95	168-302
			p-Dichlorobenzene [22]	1·42-7·79	205-358
			Benzene [12]	1·88-8·77	224-362
			Naphthalene [23, 19]	1·60-8·00	161-236
			p-Xylene [12]	0·78-3·53	194-260
			p-Chlorotoluene [12]	0·34-2·17	193-290
			p-Bromotoluene [12]	0·35-2·12	219-312
			p-Iodotoluene [12]	0·18-3·88	152-353
			p-Nitrotoluene [12]	1·71-9·11	183-220
			Methyl *p*-toluate [12]	2·55-10·95	174-177
Methyl *p*-hydroxybenzoate	$C_6H_4(OH).COOCH_3$	153	Naphthalene [22, 23, 24, 25]	1·26-14·72	178-318
			p-Azoxyanisol [24]	0·50-1·415	151-148
			Dimethyloxalate [24]	1·01-9·02	149-167
			Nitrobenzene [22]	0·78-1·80	175-193

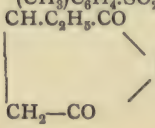
			m-Dinitrobenzene [22]	1·02-6·18	146-178
			p-Nitrotoluene [22]	0·90-7·87	164-210
			2·4-Dinitrotoluene [22]	0·90-6·47	161-200
			2·4·6-Trinitrotoluene [22]	0·50-5·63	153-191
			p-Chloronitrobenzene [22]	1·10-6·12	159-202
			p-Dichlorobenzene [22]	0·60-1·70	205-264
			p-Chlorobromobenzene [22]	0·28-0·78	167-217
			p-Dibromobenzene [22]	1·28-7·24	199 391
			Benzil [22]	1·23-6·65	152-178
Ethyl *p*-hydroxybenzoate	$C_6H_4(OH).COOC_2H_5$	166	Naphthalene [19]	0·78-13·79	194-325
Phenyl salicylate	$C_6H_4(OH).COOC_6H_5$	214	Benzene [15]	1·40-11·00	241-257
Methyl 3-chloro-*p*-hydroxybenzoate	$C_6H_3(OH).Cl.COOCH_3$	186·5	Naphthalene [24]	0·88-7·80	186-224
Methyl 3-bromo-*p*-hydroxybenzoate	$C_6H_3(OH).Br.COOCH_3$	231	Naphthalene [24, 25]	0·81-10·24	231-271
Methyl 3-iodo-*p*-hydroxybenzoate	$C_6H_3(OH).I.COOCH_3$	278	Naphthalene [24]	1·09-6·54	299-314
Methyl 3·5-dichloro-*p*-hydroxybenzoate	$C_6H_2(OH).Cl_2.COOCH_3$	221	Naphthalene [25]	1·23-10·30	203-249
Methyl 3·5-dibromo-*p*-hydroxybenzoate	$C_6H_2(OH).Br_2.COOCH_3$	310	Naphthalene [20]	1·20-11·18	294-323
Methyl 3·5-di-iodo-*p*-hydroxybenzoate	$C_6H_2(OH).I_2.COOCH_3$	404	Naphthalene [20]	1·23-9·76	402-406
Methyl 3-nitro-*p*-hydroxybenzoate	$C_6H_3(OH).NO_2.COOCH_3$	197	Naphthalene [25]	0·97-9·14	191-204
Ethyl *m*-nitro-salicylate	$C_6H_3(OH).NO_2.COOC_2H_5$	211	Naphthalene [19]	0·82-7·38	211-221
Ethyl *m*-nitro-*p*-hydroxybenzoate	$C_6H_2(OH).NO_2.COOC_2H_5$	211	Naphthalene [19, 23]	0·64-14·28	219-243
Methyl amido-*p*-hydroxybenzoate	$C_6H_3(OH).NH_2.COOCH_3$	167	Naphthalene [19]	0·92-7·09	179-340
Methyl 6-hydroxy *o*-toluate	$C_6H_3(OH).(CH_3).COOCH_3$	166	Naphthalene [19, 25]	0·45-7·22	163-211
Methyl 3-hydroxy *p*-toluate	$C_6H_3(OH).(CH_3).COOCH_3$	166	Naphthalene [19]	0·57-9·71	171-175
Methyl 4-hydroxy *m*-toluate	$C_6H_3(OH).(CH_3).COOCH_3$	166	Naphthalene [19]	0·76-11·24	163-175
Methyl 2-hydroxy *m*-toluate	$C_6H_3(OH).(CH_3).COOCH_3$	166	Naphthalene [19]	0·62-9·93	164-174
Methyl 4-hydroxy *o*-toluate	$C_6H_3(OH).(CH_3).COOCH_3$	166	Naphthalene [19]	0·54-8·76	152-240
Dimethyl sulphate	$(CH_3)_2SO_4$	126	Acetic acid [135, 22]	2·41-3·96	138·4-139
			Benzene [135, 22]	2·01-4·18	120·8-132·5
Methyl pyrophosphate	$(CH_3)_4P_2O_7$	234	Methyl iodide [113]	0·131 0·189	239-264·9
Methyl hypophosphate	$(CH_3)_2PO_3$	109	Methyl iodide [113]	0·220-0·305	133·5 141·6
Ethyl hypophosphate	$(C_2H_5)_2PO_3$	137	Ethyl iodide [113]	0·280-0·351	144·7-144·8

OXIMES.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Aldoxime	$CH_3CH : NOH$	59	Diphenylamine [29]	0·405-9·891	84·48-155·1
			Benzophenone [29]	0·331-3·185	71·83-84·05
			Stearin [29]	0·801-8·264	56·96-59·16
			Azobenzene [29]	0·339-3·340	64·83-84·80
			p-Toluidine [29]	0·507-54·93	68·39-68·25
			Cetyl alcohol	0·810-3·598	61·10-66·16
Acetoxime	$(CH_3)_2 C : NOH$	73	Acetic acid [8, 55]	0·284-20·23	71·5-77·3
			Benzene [8]	0·219-42·89	104-195
			Water [8]	0·960-19·35	76·5-88·3
Benzaldoxime	$C_6H_5.CH : NOH$	121	Benzene [8]	0·439-39·70	134-294
			Acetic acid [8]	0·455-27·90	113-132
			Naphthalene [11]	1·01-9·49	124-181
o-Nitrobenzaldoxime	$C_6H_4 (NO_2) CH : NOH$	166	Naphthalene [11]	1·06-5·96	171-209
p-Nitrobenzaldoxime	$C_6H_4(NO_2) CH : NOH$	166	Naphthalene [11]	1·14-9·41	170-209
Benzaldoxime ethylether	$C_6H_5.CH : NO.C_2H$	149	Benzene [8]	0·468-35·17	138-182
			Acetic acid [8]	0·833-28·10	132-166
Acetophenoneoxime	$C_6H_5.C.(CH_3) : NOH$	135	Benzene [8, 14]	0·625-40·59	169-279
			Acetic acid [8]	1·517-23·81	134-158
			Ether [18]	2·21	137
			Ethyl alcohol [14]	1·55-12·97	129-154
			Cyclohexane [125]	0·49-2·34	219·5-258·3
Benzophenoneoxime	$(C_6H_5)_2.C : NOH$	197	Acetic acid [8]	0·725-15·55	175-222
			Benzene [8]	0·238-15·88	211-260
o-Amidobenzophenoneoxime	$NH_2C_6H_4.C (C_6H_5) : NOH$	232	Benzene [1]	0·22-0·78	187-253
α-Benzilmonoxime	$C_6H_5C : (NOH) CO.C_6H_5$	225	Benzene [1]	0·07-0·80	179-270
β-Benzilmonoxime	$C_6H_5C : (NOH) CO.C_6H_5. + \frac{1}{2} C_6H_6$	264	Benzene [1]	0·65-3·89	278-356
Carvoxime	$C_{10}H_{14} : NOH$	165	Cyclohexane [125]	0·38-4·80	290·5-335·8
Camphoroxime	$C_{10}H_{16} : NOH$	167	Benzene [13]	1·43-13·41	228-305
			Cyclohexane [125]	0·24-3·96	215·8-324·4
			p-Dibromobenzene [13]	0·98-8·48	200-276
			m-Dinitrobenzene [13]	0·50-7·05	151-227
			Methyl *p*-toluate [13]	1·29-8·95	306-291
			Acetic acid [8]	0·880-45·31	164-200
d-Camphoroxime		167	Benzene [1, 8]	0·27-3·62	182-286
l-Camphoroxime		167	Benzene [8]	5·16-13·35	229-308

AMIDES.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Acetamide	$CH_3.CONH_2$	59	Acetone [56]	31·2-74·3 (N)	62·6-72·9
Thioacetamide	$CH_3.CSNH_2$	75	Naphthalene [11]	0·92-2·84	80-98
iso-Butylacetamide	$CH_2(C_4H_9).CONH_2$	115·1	Water [57]	6·250-7·597	174-178
			Ethyl alcohol [56]	22·6-50·7 (N)	115·7-107·7
			Acetone [56]	34·3-66·5 (N)	117-125
			Chloroform [56]	23 2-31·8 (N)	146-157
			Ether [56]	9·6-11·6 (N)	145-156
			Benzene [56]	19·0-44·2 (N)	148-191
Phenylacetamide	$CH_3(C_6H_5).CONH_2$	135·1	Water [57]	5·346-12·04	156-207
			Ethyl alcohol [56]	25·4-5·83 (N)	132-134
			Acetone [56]	28·8-51·0 (N)	143-151
			Chloroform [56]	20·3-31·0 (N)	154-167
Diphenoxyacetamide	$(C_6H_5O)_2$ CH.$CONH_2$	243	Benzene [12]	0·40-1 52	264-343
Benzylacetamide	CH_3CONH ($C_6H_5CH_2$)	149	Naphthalene [58]	1·53-8·41	148-218
o-Nitrobenzylacetamide	$NO_2.C_6H_4.CH_2.NH.COCH_3$	194	Naphthalene [58]	1·95-13·24	189-285
p- ,,			Naphthalene [68]	2·01-9·42	188-279
Propionamide	$C_2H_5.CONH_2$	73·1	Water [57]	5·496-11·68	83·3-84·5
			Ethyl alcohol [56]	42·4-80·7 (N)	79·6-80·7
			Acetone [56]	33·8-68·7 (N)	76·3-84·4
			Chloroform [56]	25·5-63·2 (N)	95·7-110 4
			Ether [56]	11·3-12·9 (N)	77·4-89·9
			Benzene [56]	21·4-56·7 (N)	112-155
n-Butyramide	$C_3H_7.CONH_2$	87·1	Water [57]	4·337-7·099	97·4-104·6
			Ethyl alcohol [56]	30·6-58·1 (N)	84·8-86·6
			Acetone [56]	28·2-58·9 (N)	91·2-96·8
			Chloroform [56]	39·2-59·6 (N)	110·1 115·6
			Benzene [56]	25·8-50·7 (N)	137-168
iso-Butyramide			Water [57]	4·485-7·456	102·7-104·8
			Ethyl alcohol [56]	27·9-66·0 (N)	84-88·6
			Acetone [56]	29·1-70·3 (N)	89·6-103·9
			Chloroform [56]	32·5-52·6 (N)	106·8-115·6
			Benzene [56]	25·2-49 8 (N)	128-165
Valeramide	$C_4H_9.CONH_2$	101·1	Water [57]	5·034-9·198	123-136

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
iso-Valeramide			Ethyl alcohol [56]	27·4-71·1 (N)	98·1-94·2
			Acetone [56]	28·5-50·1 (N)	99·7-106·4
			Chloroform [56]	32·3-53·7 (N)	132-141
			Benzene [56]	22·1-53·2 (N)	142-183
Glycollamide	$CH_2OH.CONH_2$	75	Acetone [56]	11·5-16·8 (N)	73·1-81·4
			Ethyl alcohol [56]	32·7-65·2 (N)	77·4-79·3
			Water [57]	3·736-6·699	80·7-73·6
Lactamide	$CH_3CH(OH).CONH_2$	89·1	Water [57]	7·734-13·14	9·34-9·54
			Ethyl alcohol [56]	28·8-52·4 (N)	90·1-93·9
			Acetone [56]	28·9-49 8 (N)	98·4-111·6
Urea	$CO(NH_2)_2$	60	Acetic acid [52]	1·48	67
			Ethyl alcohol [14, 38]	1·32-2·64	62-63·5
			Water [14, 7]	1·32-16·59	72-74
Phenyl carbamide	$NH_2.CO.NH.C_6H_5$	136	Water [57]	2·815-5·371	141-159
			Ethyl alcohol [56]	38·2-75·8 (N)	155-164
			Acetone [56]	21·7-42·4 (N)	147-168
Diphenyl carbamide	$(C_6H_5NH)_2CO$	212	Acetone [56]	10·0-13·0 (N)	206-220
			Ethyl alcohol [56]	8·0-8·7 (N)	207-196
Benzamide	$C_6H_5.CONH_2$	121	Acetic acid [52]	2·00	126
			Naphthalene [55]	1·13-7·86	134-231
Thio-benzamide	$C_6H_5.CSNH_2$	137	Naphthalene [11]	0·95-9·65	132-197
Acetyl benzamide	$C_6H_5.CONH.COCH_3$	163	*p*-Dibromobenzene [68]	2·813-8·597	215-257
Acetyl salicylamide	$C_6H_4(OH).CONH.COCH_3$	179	*p*-Dibromobenzene [68]	1·321-4·999	231-270
Benzoyl salicylamide	$C_6H_5.COOC_6H_4.CONH_2$	241	*p*-Dibromobenzene [68]	0·964-3·343	295-348
Benzene sulphonamide	$C_6H_5SO_2NH_2$	157	Naphthalene [58]	0·90-2·11	166-203
p-Toluene sulphonamide	$(CH_3)C_6H_4.SO_2.NH_2$	171	Naphthalene [58]	1·50-4·12	175-238
Ethyl succinimide		127	*p*-Bromotoluene [9]	0·980-45·71	127·7-274·5

ANILIDES.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Formanilide	$C_6H_5NH.COH$	121	Benzene [13, 1, 56]	1·26-11·20	149-343
			p-Xylene [13]	1·37-12·87	176-409
			p-Chlorotoluene [13]	0·67-7·69	162-342
			p-Brom. toluene [13]	0·58-6·57	160-345
			p-Iodotoluene [13]	0·84-8·41	171-397
			p-Nitrotoluene [13]	1·28-6·16	147-178
			p-Toluidine [13]	2·17-10·10	128-131
			Methyl *p*-toluate [13]	1·90-14·42	140-197
			p-Dichlorbenzene [13]	1·49-10·59	174-338
			p-Dibrom. benzene [13]	1·50-12·05	164-343
			Water [57]	4·561-9·026	161-194
			Naphthalene [58]	1·13-12·08	128-213
			Dimethyl oxalate [24]	0·96-8·65	137-152
			Ethyl alcohol [56]	32·4-68·8 (N)	116·6-119·6
			Acetone [56]	23·5-42·8 (N)	117-121
			Chloroform [56]	27·7-53·2 (N)	155-170
			Ether [56]	18·2-22·2 (N)	135-145
Thioformanilide	$C_6H_5NH.CSH$	137	Benzene [12]	0·38-0·77	144-157
o-Chloroformanilide	C_6H_4 (Cl) NH.COH	155·5	Naphthalene [58]	1·55-10·25	151-188
p-Chloroformanilide	C_6H_4 (Cl) NH.COH	155·5	Naphthalene [58]	1·51-7·97	150-210
p-Bromoformanilide	C_6H_4 (Br) NH.COH	200	Naphthalene [58]	1·79-9·33	190-258
o-Nitroformanilide	C_6H_4 (NO_2) NH.COH	166	Naphthalene [58]	1·58-9·62	165-179
m-Nitroformanilide	C_6H_4 (NO_2) NH.COH	166	Naphthalene [58]	1·64-5·01	166-200
p-Nitroformanilide	C_6H_4 (NO_2) NH.COH	166	Naphthalene [58]	0·84-0·94	162-164
Acetanilide	$C_6H_5NH.COCH_3$	135	Sulphur dioxide [69]	8·94-9·93	137·7-135·0
			Acetic acid [28]	1·17-1·97	154-157
			Benzene [14, 38]	1·45-9·68	160-293
			Ethyl alcohol [14, 53, 38]	1·49-13·52	139-159
			Naphthalene [58]	1·57-13·74	146-274
			Dimethyloxalate [24]	1·00-8·93	165-184
			Anisol [70]	1·054-4·866	173·0-176·7
Thioacetanilide	$C_6H_5NH.CS.CH_3$	151	Naphthalene [11]	1·01 8·89	145-202
o-Chloroacetanilide	C_6H_4 (Cl) NH.$COCH_3$	169·5	Naphthalene [58]	0·65-1·71	145-156

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
m-Chlor. acetanilide	C_6H_4 (Cl) $NH.COCH_3$	169·5	Naphthalene [58]	1·73-15·79	164-316
p-Chlor. acetanilide	C_6H_4 (Cl) $NH.COCH_3$	169·5	Naphthalene [58]	1·27-2·11	143-150
m-Brom. acetanilide	C_6H_4 (Br) $NH.COCH_3$	214	Naphthalene [58]	2·23-18·29	207-390
p-Brom. acetanilide	C_6H_4 (Br) $NH.COCH_3$	214	Naphthalene [58]	2·13-4·26	213-237
o-Nitroacetanilide	C_6H_4 (NO_2) $NH.COCH_3$	180	Naphthalene [58]	1·97-11·89	176-192
m-Nitroacetanilide	C_6H_4 (NO_2) $NH.COCH_3$	180	Naphthalene [58]	1·69-3·10	177-213
p-Nitroacetanilide	C_6H_4 (NO_2) $NH.COCH_3$	180	Naphthalene [58]	0·32-0·76	164-190
Methyl acetanilide	$C_6H_5N.(CH_3).COCH_3$	149	Water [57]	7·898-17·33	434-627
			Acetone [56]	23·8-45·6 (N)	141-144
			Ethyl alcohol [56]	31·8-78·2 (N)	146-150
			Chloroform [56]	13·0-28·0 (N)	135-142
			Ether [56]	20·4-29·6 (N)	152-155·5
			Benzene [56]	23·2-45·8 (N)	151-155
			Cyclohexane [125]	0·30-0·69	135·6-143·6
Ethyl acetanilide	$C_6H_5N.(C_2H_5).COCH_3$	163	Ethyl alcohol [56]	23·8-56·6 (N)	154-158
			Acetone [56]	20·6-41·1 (N)	162-165
			Chloroform [56]	20·1-26·4 (N)	137-148
			Ether [56]	31·5-42·0 (N)	169-173
			Benzene [56]	19·8-43·2 (N)	156-164
Propioanilide	$C_6H_5NH.COC_2H_5$	149	Naphthalene [58]	1·46-14·97	146-266
Butyranilide	$C_6H_5NH.COC_3H_7$	163	Naphthalene [58]	1·75-17·84	171-294
iso-Butyranilide	$C_6H_5NH.COC_3H_7$	163	Naphthalene [58]	1·76-12·14	160-251
iso-Valeranilide	$C_6H_5NH.COC_3H_9$	177	Naphthalene [58]	1·81-17·63	188-308
Palmitinanilide	$C_6H_5NH.COC_{15}H_{31}$	331	Naphthalene [58]	3·28-26·63	337-460
Stearinanilide	$C_6H_5NH.COC_{17}H_{35}$	359	Naphthalene [58]	3·54-27·88	358-479
Glycollanilide	$C_6H_5NH.COCH_2$ OH	151	Water [57]	4·591-8·095	175-197
			Ether [56]	7·8-9·7 (N)	152-168
			Benzene [56]	11·7-28·7 (N)	185-254
			Chloroform [56]	23·4-35·8 (N)	242-305
			Acetone [56]	25·4-45·7 (N)	153-157
			Ethyl alcohol [56]	24·8-48·0 (N)	145-154
Lactanilide	$C_6H_5NH.COCH(OH).CH_3$	165	Water [57]	6·071-11·04	208-245
			Ethyl alcohol [56]	25·5-53·1 (N)	158-166
			Chloroform [56]	18·7-28 3 (N)	206-242

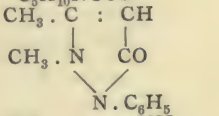
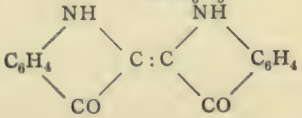
Benzanilide	$C_6H_5NH.COC_6H_5$	197	Ether [56]	25·8-32·1 (N)	206-220
			Benzene [56]	12·8-32·5 (N)	201-269
			Ethyl alcohol [142]	14·8-22·6 (N)	186-185
			Aniline [37]	1·19-6·75	190-196
			Benzoylcyclohexylamine [128]	1·49-4·08	336-300
			Benzene [1, 142]	0·17	241
			Naphthalene [58]	1·79-5·83	185-223
			Chloroform [142]	24·0-39·2 (N)	207-205·5
			Dimethyl oxalate [24]	1·05-3·11	227-226
			Acetone [142]	30·5-43·2 (N)	187-189
o-Methoxybenzanilide	$C_6H_5NH.COC_6H_4OCH_3$	227	Naphthalene [11]	1·86-8·78	225-257
o-Nitrobenzanilide	$C_6H_5NH.COC_6H_4NO_2$	242	Naphthalene [11]	1·04-4·39	245-291
m-Nitrobenzanilide	$C_6H_5NH.COC_6H_4NO_2$	242	Naphthalene [11]	1·01-8·89	236-323
Formo *o*-toluide	C_6H_4 (CH_3) NH.COH	135	*p*-Dibrombenzene	0·58-5·21	175-231
			p-Dichlorbenzene [13]	1·07-8·75	184-271
			Methyl *p*-toluate [13]	2·54-10·62	159-197
			p-Nitrotoluene [13]	1·23-7·15	155-194
			p-Iodotoluene [13]	0·88-10·18	179-395
			p-Xylene [13]	1·14-6·30	196-272
			Benzene [13]	0·37-7·37	142-266
Formo-*p*-toluide	C_6H_4 (CH_3) NH.COH	135	*p*-Chlorotoluene [13]	0·79-4·63	187-257
			p-Bromotoluene [13]	0·78-5·51	222-298
			Benzene [13]	0·38-13·78	128-374
			p-Xylene [12]	1·01-6·39	168-312
			p-Chlorotoluene [13]	0·73-5·58	171-309
			p-Bromotoluene [13]	0·62-4·31	232-330
			p-Iodotoluene [13]	1·63-7·43	274-427
			p-Nitrotoluene [13]	1·38-8·92	164-212
			Methyl *p*-toluate [13]	1·89-11·80	144-197
3-Nitro 4-Formotoluide	C_6H_3 (CH_3) (NO_2) NH.COH	180	Naphthalene [58]	1·81-10·32	172-195
2-Nitro 4-Formotoluide	C_6H_3 (CH_3) (NO_2) NH.COH	180	Naphthalene [58]	1·87-9·66	178-258
3-Nitro 6-Formotoluide	C_6H_3 (CH_3) (NO_2) NH.COH	180	Naphthalene [58]	1·97-3·96	182-204
o-Acettoluide	C_6H_4 (CH_3) NH.$COCH_3$	149	Naphthalene [58]	2·41-13·95	171-268
m-Acettoluide	C_6H_4 (CH_3) NH.$COCH_3$	149	Naphthalene [58]	1·39-9·59	157-270
p-Acettoluide	C_6H_4 (CH_3) NH.$COCH_3$	149	Naphthalene [58]	1·50-9·98	148-308
3-Nitro 4-Acettoluide	$C_6H_3(CH_3)$ (NO_2).NH.$COCH_3$	194	Naphthalene [58]	1·94-11·23	186-200
			Benzene [58]	0·80-11·60	193-219

Substance.	Formula.	M.W. (Calcd.)	Solvent.	Concentration.	M.W. (Obs.).
o-Nitrobenzo-*o*-toluide	$C_6H_4(CH_3)NH.CO.C_6H_4(NO_2)$	256	Naphthalene [11]	0·69-2·75	247-299
m-Nitrobenzo-*o*-toluide	$C_6H_4(CH_3)NH.CO\,C_6H_4(NO_2)$	256	Naphthalene [11]	1·02-7·45	270-315
Benzo-*o*-nitrotoluide	$C_6H_4(NO_2)NH.CO(C_6H_5)$	242	Naphthalene [11]	1·03-6·14	246-248
o-Nitrobenzo nitrotoluide	$C_6H_4(NO_2)NH.CO\,C_6H_4(NO_2)$	287	Naphthalene [11]	3·16-5·28	307-300
Ethoxy-*m*-toluithioanilide	$C_6H_5.NH.CS.C_6H_3(CH_3)(OC_2H_5)$	271	Naphthalene [11]	1·09-9·07	277-300
Tartaric-*di*-toluide	$[CH(OH).CO.NH.C_6H_4(CH_3)]_2$	328	Pyridine [32]	1·23-3·67	331-354
m-Formoxylide	$(CH_3)_2\,C_6H_3NH.CHO$	149	Benzene [12]	0·32-0·88	180 201
p-Formoxylide	$(CH_3)_2\,C_6H_3NH.CHO$	149	Benzene [12]	0·23-1·04	163-207
m-Acetoxylide	$C_6H_3(CH_3)_2\,NH.CO\,CH_3$	163	Naphthalene [58]	1·58-18·02	165-273
			Benzene [1]	0·18-0·36	142-173
Formo-*p*-anisidide	$C_6H_4(OCH_3)NH.CO\,H$	151	*p*-Chlorotoluene [13]	0·44-0·86	210-234
			p-Bromtoluene [13]	0·49-1·75	192-261
			p-Iodotoluene [13]	0·34-1·99	172-261
			p-Nitrotoluene [13]	1·50-12·06	180-250
			Methyl-*p*-toluate [13]	1·85-12·54	188-253
o-Acetanisidide	$C_6H_4(OCH_3)NH.CO\,CH_3$	165	Naphthalene [58]	1·78-13·22	164-194
p-Acetanisidide	$C_6H_4(OCH_3)NH.CO\,CH_3$	165	Naphthalene [58]	1·61-17·14	176-358
Benzo-*o*-anisidide	$C_6H_5.CO\,NH.C_6H_4(OCH_3)$	227	Naphthalene [11]	1·09-6·17	222-233
Benzo-*p*-anisidide	$C_6H_5.CO\,NH.C_6H_4(OCH_3)$	227	Naphthalene [11]	1·86-8·78	225-251
Anisithioanilide	$C_6H_5NH.CSC_6H_4OCH_3$	243	Naphthalene [11]	1·00-9·20	238-276
Acet-pseudocumide	$C_6H_2(CH_3)_3\,NH.COCH_3$	177	Naphthalene [11]	1·79-6·67	185-263
p-Formyl phenetidin	$C_2H_5OC_6H_4N:CHOH$	165	Benzene [12]	0·40-4·81	171-300
p-Acet-phenetidide	$C_2H_5OC_6H_4NH.COCH_3$	179	Naphthalene [58]	1·72-11·81	188-321

AMINES.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Ethylamine	$C_2H_5NH_2$	45·07	Water [17]	3·915-7·473	45·7-4·468
			Benzene [17]	1·595-5·360	57·1-59·3
Propylamine	$C_3H_7NH_2$	59·1	Water [17]	2·329-5·147	56·5-63·0
Di-*iso*-butylamine	$(C_4H_9)_2NH$	129·2	Formamide [42]	0·897-1·813	145·153
iso-amylamine	$C_5H_{11}NH_2$	87·1	Water [17]	0·921-7·114	84·8 88·2
			Benzene [71]	1·940-9·149	88·9-104·1
Benzylamine	$C_6H_5CH_2NH_2$	107·1	Benzene [71]	2·752-9·324	110·4-122·9
			Water [71]	1·326-5·511	105·5-134·4

Aniline	$C_6H_5NH_2$	93·1	Water [17]	1·976-3·891	100·2-107·4
			Benzene [17]	1·828-8·828	104·5-121·5
			Nitrobenzene [5]	0·5723-21·4049	80·5-121
			Ether [18]	1·826-2·153	93·5-93·4
			Naphthalene [58]	1·20-6·59	94-102
			Cyclohexane [21]	0·40-3·05	106-136
			p-Bromotoluene [9]	0·338-46·011	86·7-226·1
m-Nitro aniline	$(NO_2)C_6H_4NH_2$	138	Bromoform [4]	0·2021-5·4193	87·3-94·1
			Water [17]	1·735-2·153	174-174
			Benzene [17]	2·617-7·243	140-164
p-Nitroso methyl aniline	$(NO)\ C_6H_4NH.CH_3$	136	Naphthalene [58]	1·41-10·03	139-160
p-Nitroso ethyl aniline	$(NO)\ C_6H_4\ NH.C_2H_5$	150	Naphthalene [24]	1·19-6·88	152-197
p-Nitroso dimethyl aniline	$(NO)\ C_6H_4\ N(CH_3)_2$	150	Naphthalene [24]	1·24-7·91	159-206
p-Nitroso diethyl aniline	$(NO)\ C_6H_4\ N(C_2H_5)_2$	178	Naphthalene [24]	1·08-7·57	151-177
Diphenylamine	$(C_6H_5)_2\ NH$	169·1	Ethyl alcohol [17]	1·53-11·40	183-222
			Hexane [133]	8·678-13·62	190-206
			Stearic acid [29]	0·603-32·69	181-210
			Benzonitrile [129]	2·359-28·03	175·6-205·5
p-Nitroso diphenylamine	$C_6H_5NH.C_6H_4(NO)$	198	Acetonitrile [129]	0·63-1·17	233-228
p-Toluidine	$C_6H_4\ (CH_3)\ NH_2$	107	Naphthalene [24]	1·45-7·74	125-133
p-Anisidine	$C_6H_4\ (OCH_3)\ NH_2$	123	Naphthalene [58]	1·25-8·57	203-251
α-Nitroso *β*-Naphthylamine	$(NO)\ C_{10}H_6\ NH_2$	172	Naphthalene [58]	1·05-7·94	95-112
Benzoylcyclohexylamine	$C_6H_5CONH.C_6H_{11}$	203	Naphthalene [24]	1·23-11·27	111-140
Pyrrole	C_4H_4NH	67	Benzanilide [128]	0·70-5 14	180-227
			Cyclohexane [21]	1·91-4·49	184-194
			Benzene [50]	0·64-2·07	84-113
N-Methyl pyrrole	$C_4H_4N.(CH_3)$	81	Acetic acid [50]	0·368-10·23	89-109
			Benzene [50]	0·370-56·82	64-95
N-Ethyl pyrrole	$C_4H_4N.(C_2H_5)$	95	Acetic acid [50]	0·245-7·006	79-85
			Benzene [50]	0·840-27·65	81-111
α-Acetyl pyrrole	$CH_3.CO.C_4H_3NH$	109	Acetic acid [50]	0·361-7·70	87-94
			Benzene [50]	0·248-29·86	96-132
α-*β*-Dimethyl pyrrole	$(CH_3)_2.C_4H_2.NH$	95	Acetic acid [50]	0·229-79·56	111-176
			Benzene [50]	0·333-17·72	112-121
Tetra-iodo pyrrole	C_4I_4NH	571	Acetic acid [50]	0·472-16·83	90-127
			Acetic acid [50]	0·368-14·52	98-119
				0·404	523

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
			Ethylene bromide [50]	0·069-2·430	545-719
Pyridine	C_5H_5N	79	Cyclohexane [21]	0·80-2·93	109-114
			p-Bromotoluene [9]	0·397-30·52	110·2-147·9
			Bromoform [4]	0·535-4·30	220·2-87·7
			Nitrobenzene [5]	2·485-17·35	87·4-100·7
Piperidine	$C_5H_{11}N$	85	Naphthalene [11]	0·91-5·16	93-100
			Water [72]	4·385-2·755	73·66-87·0
			Nitrobenzene [5]	3·4977-24·06	113-143
Formyl-piperidine	$C_5H_{10}NCOH$	113	Benzene [12]	0·55-7·67	108-122
Antipyrine		188	Benzene [1, 12]	0·28-1·23	237-264
Indigo		262	*p*-Toluidine [73]	0·21-0·31	468·7-514·4

NITROSO COMPOUNDS.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Dimethylnitrosoamine	$(CH_3)_2$ N.NO	74	Benzene [1]	0·28-2·30	72-80
Diethylnitrosoamine	$(C_2H_5)_2$ N.NO	102	Benzene [1]	0·24-4·79	91-109
Nitrosoethylaniline	$C_6H_5N(C_2H_5)$ NO	150	Benzene [1]	2·34-6·43	141-149
Nitrosodimethylaniline	(NO) C_6H_4N $(CH_3)_2$	150	Benzene [1]	0·19-3·17	118-182
Nitrosodiethylaniline	(NO) C_6H_4N $(C_2H_5)_2$	178	Benzene [1]	0·30-5·82	163-227
Nitroso 2·5-xylene	(NO) C_6H_3 $(CH_3)_2$	135	Benzene [132]	1·105-2·50	129·5-133·3
Nitroso 2·4-xylene	(NO) C_6H_3 $(CH_3)_2$	135	Benzene [132]	1·24-2·63	232·2-246
Nitroso 2·6-xylene	(NO) C_6H_3 $(CH_3)_2$	135	Acetone [132]	1·76-4·90	187-194·1
Nitroso 2·4·6-mesitylene	(NO) C_6H_2 $(CH_3)_3$	149	Benzene [132]	1·64-3·26	232·0-240·4
			Acetone [132]	6·55	180·4

URETHANES.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Urethane	$NH_2.CO.OC_2H_5$	89·1	Naphthalene [11]	0·98-9·41	98-167
			Water [57]	2·084-5·338	91-88·4
			Benzene [56]	30·2-58·4 (N)	129-140
			Ethyl alcohol [56]	35·3-89·4 (N)	94·6-91·1
			Stearic acid [29]	1·066-23·26	99·74-125·3
			Acetone [56]	26·5-49·2 (N)	92·0-95·6
			Chloroform [56]	31·2-54·1 (N)	106·9-112·1
			Ether [56]	25·8-30·6 (N)	100·5-104·2
Phenylurethane	$C_6H_5NH.CO.OC_2H_5$	165	Ethyl alcohol [56]	26·7-55·6 (N)	162-168
			Acetone [56]	24·5-51·4 (N)	154-160
			Chloroform [56]	21·2-32·7 (N)	171·5-179
			Ether [56]	28·7-45·1 (N)	169-172
			Benzene [56, 1]	23·9-49·3 (N)	171-172
			Naphthalene [11]	0·97-8·89	175-194
Methyl carbamate	$NH_2CO.OCH_3$	75	Benzene [1]	0·28-1·05	83-102
Phenylxanthogenamide	$C_6H_5N.C(SH).OC_2H_5$	181	Benzene [1]	0·35-7·35	154-216

NITRILES.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Valeryl acetonitrile	$(CH_3)_3.C.CO.CH_2CN$	125	Benzene [137]	0·62-6·89	124·1-175·3
Salicylnitrile	$C_6H_4(OH)CN$	119	Naphthalene [20]	0·50-8·02	125-251
5-Bromosalicylnitrile	$C_6H_3(OH)Br.CN$	198	Naphthalene [74]	0·437-2·734	195-228
3·5-Dibromosalicylnitrile	$C_6H_2(OH)Br_2CN$	277	Naphthalene [74]	0·483-2·913	296-288
6-Nitrosalicylnitrile	$C_6H_3(OH)(NO_2)CN$	164	Naphthalene [74]	0·278	181
3·5-Dinitrosalicylnitrile	$C_6H_2(OH)(NO_2)_2CN$	209	Naphthalene [74]	0·458-2·850	202-207
3-Nitro 5-bromosalicylnitrile	$C_6H_2(OH)Br(NO_2)CN$	243	Naphthalene [74]	0·40-2·808	249-242
Salicylnitrilebenzyl ether	$C_7H_7O.C_6H_4CN$	209	Naphthalene [74]	0·977 6·014	212-217

KETONES.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Acetone	$(CH_3)_2$ CO	58	Benzene [8]	0·475-13·98	57·2-71·0
			Acetic acid [8]	0·502-15·91	57·6-63·7
			Water [8]	6·62-18·52	56·9-61·8
			Cyclohexane [127]	0·84-2·84	78·2-88·5
			Dicyclohexane [124]	1·47-6·95	68·2-171·6
Acetyl acetone	$CH_3.CO.CH_2.CO.CH_3$	100	Benzene [1]	0·25-6·95	103-101
			Cyclohexane [127]	0·59-2·50	106-111·1
Methyl ethyl ketone	$CH_3.CO.C_2H_5$	72	Cyclohexane [127]	0·95-2·10	85·2-93·3
Acetophenone	$CH_3.CO.C_6H_5$	120	Antimony trichloride [75]	0·41-3·65	123-116
			Acetic acid [52]	1·86	130
			Benzene [8]	0·957-30·17	115-136
			Acetic acid [8]	0·655-39·11	124-156
			Cyclohexane [127]	0·41-10·72	121-198·2
			Dicyclohexyl [124]	0·99-8·69	109·3-246·0
p-Hydroxyacetophenone	C_6H_4 (OH) $CO.CH_3$	136	Naphthalene [24]	2·10-8·72	147-200
p-Hydroxypropiophenone	C_6H_4 (OH) $CO.C_2H_5$	150	Naphthalene [24]	1·89-8 01	163-226
p-Hydroxyvalerophenone	C_6H_4 (OH) $CO.C_4H_9$	178	Naphthalene [24]	1·71-8·81	203-327
p-Hydroxypalmitophenone	C_6H_4 (OH) $CO.C_{15}H_{31}$	332	Naphthalene [24]	1·54-7·69	344-541
Benzophenone	$C_6H_5CO.C_6H_5$	182	Ether [18]	2·70	189
			Cyclohexane [127]	0·47-5·35	195·8-217·8
			Carbon disulphide [14]	1·62-3·21	182-187
			Antimony trichloride [75]	0·60-2·20	191-176
p-Hydroxybenzophenone	C_6H_4 (OH) $CO.C_6H_5$	198	Naphthalene [24]	1·89-7·85	209-246
Dihydroxybenzophenone	C_6H_3 $(OH)_2$ $CO.C_6H_5$	214	Benzene [1]	0·10-0·49	234-244
Trihydroxybenzophenone	C_6H_2 $(OH)_3$ $CO.C_6H_5$	230	Benzene [1]	0·11	232
m-Nitro *p*-hydroxybenzophenone	C_6H_4 (OH) $CO.C_6H_4$ (NO_2)	243	Naphthalene [24]	1·87-7·93	246-272
p-Nitro *p*-hydroxybenzophenone	C_6H_4 (OH) $CO.C_6H_4$ (NO_2)	243	Naphthalene [24]	2·06-8·67	245-326
Cyclohexanone	$C_6H_{10}O$	98	Dicyclohexyl [124]	1·07-7·47	106·8-199·8
			Cyclohexane (cryos.) [127]	0·364-6·28	454·5-560·3
			Cyclohexane (ebul.) [127]	1·21-6·25	151·4-153·7
			Benzene (cryos.) [127]	0·69-5·97	98·0-102·1

			Benzene (ebul.) [127]	0·82-4·34	97·1-103·6
			p-Xylene [127]	0·76-6·62	99·0-107·8
o-Methylcyclohexanone	$C_7H_{12}O$	112	Cyclohexane [127]	0·53-9·33	175·4-212·5
p-Methylcyclohexanone	$C_7H_{12}O$	112	Cyclohexane [127]	0·69-10·85	155·0-191·6

ALDEHYDES.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Formaldehyde	H.CHO	30	Water [76]	2·742	34·4
Chloral	CCl_3.CHO	147·5	Benzene [8]	0·739-32·25	149-163
			Acetic acid [8]	0·763-29·92	179-162
Chloral hydrate	CCl_3.CH $(OH)_2$	165·5	Water [8]	0·887-15·19	139-144
			Benzene [8]	0·372-0·719	181-184
			Acetic acid [8]	0·267-34·07	109-151
Chloral alcoholate	CCl_3.CH (OH) OC_2H_5	193·5	Water [8]	1·113-10·69	151-160
			Benzene [8]	0·568-42·12	178-259
			Acetic acid [8]	0·574-36·37	139-192
			Water [8]	1·858-21·70	98·5-100·4
* Benzaldehyde	C_6H_5.CHO	106	Benzene [8]	0·511-17·64	102-114
			Acetic acid [8]	0·452-26·29	109-113
			Nitrobenzene [5]	0·589-24·24	81·7-135·8
			Dicyclohexyl [124]	0·85-4·02	105·0-152·0
Salicylaldehyde	C_6H_4 (OH).CHO	122	Nitrobenzene [22]	0·72-8·80	130-142
			m-Dinitrobenzene [22]	1·07-5·78	121-131
			p-Dibromobenzene [22]	1·01-5·28	116-137
			Benzil [22]	0·88-5·30	112-125
			Naphthalene [22, 23, 19]	1·00-16·40	114-154
m-Hydroxybenzaldehyde	C_6H_4HO.CHO	122	*p*-Dibromobenzene [22]	1·01-4·68	160-271
			p-Chlorobromobenzene [22]	0·33-2·53	131-241
			p-Dichlorobenzene [22]	0·68-2·94	151-241
			Naphthalene [19, 24, 23, 22]	0·41-10·30	122-221
p-Hydroxybenzaldehyde	C_6H_4HO.CHO	122	Nitrobenzene [22]	0·63-2·17	147-177
			m-Dinitrobenzene [22]	0·99-5·79	133-162
			p-Nitrotoluene [22]	0·95-8·01	142-202
			2·4-Dinitrotoluene [22]	0·93-7·63	130-186
			2·4·6-Trinitrotoluene [22]	0·92-6·75	141-201

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
			p-Chloronitrobenzene [22]	1·00-6·24	150-196
			p-Dichlorobenzene [22]	0·26-0·71	152-201
			p-Dibromobenzene [22]	1·03-7·75	207-604
			Benzil [22]	0·96-9·65	135-154
			p-Chlorobromobenzene [22]	0·31-0·91	150-254
			Naphthalene [22, 23, 19, 24, 25]	1·33-10·11	159-317
			p-Azoxyanisole [24]	0·344-0·998	125-124
3-Nitro-*p*-hydroxybenzaldehyde	C_6H_3 (OH) NO_2.CHO	167	Naphthalene [25]	1·11-8·95	164-176
3-Bromo-*p*-hydroxybenzaldehyde	C_6H_3 (OH) Br.CHO	201	Naphthalene [25]	1·76-10·22	210-259
3·5-Dichlorohydroxybenzaldehyde	C_6H_2 (OH) Cl_2.CHO	191	Naphthalene [25]	1·05-9·39	187-220
3·5-Dibromohydroxybenzaldehyde	C_6H_2 (OH) Br_2.CHO	280	Naphthalene [25]	1·02-8·50	266-307
3·5-Diiodohydroxybenzaldehyde	C_6H_2 (OH) I_2.CHO	374	Naphthalene [25]	1·08-9·91	373-418
Acetyl-*o*-Amidobenzaldehyde	C_6H_4CHO NH.$COCH_3$	163	Naphthalene [58]	1·63-8·77	160-173
Acetyl-*p*-Amidobenzaldehyde	C_6H_4CHO NH.$COCH_3$	163	Naphthalene [58]	1·63-3·50	166-202
o Homosalicylaldehyde	$C_6H_3CH_3$ (OH).CHO	136	Naphthalene [19]	0·43-5·02	139-140
o-Homo-*p*-Hydroxybenzaldehyde	$C_6H_3CH_3$ (OH).CHO	136	Naphthalene [24, 19]	0·47-3·53	133-191
m-Homo-*p*-hydroxybenzaldehyde	$C_6H_3CH_3$ (OH).CHO	136	Naphthalene [24]	0·96-7·17	154-255
Benzoylaldehyde	C_6H_5.CO.CH_2.CHO	148	Benzene [12]	0·54-0·95	101-115
p-Thymotinaldehyde	C_6H_2 (OH).CH_3.C_3H_7.CHO	178	Naphthalene [19, 24]	0·66-9·92	190-267
Vanillin	C_6H_3 (OH) OCH_3.CHO	152	Naphthalene [24, 19]	0·59-10·04	147-185
4-Hydroxy-α-Naphthaldehyde	$C_{10}H_6$ (OH).CHO	172	Naphthalene [24]	0·80-2·65	179-234

HYDROCARBONS, NITRO AND OTHER DERIVATIVES.

Substances.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Benzene	C_6H_6	78	Acetic acid [10, 8]	0·89-25·47	79·6-113·1
			Phenol [10]	1·002-27·73	81·1-117·8

Naphthalene	$C_{10}H_8$	128	Acetic acid [8]	0·455-6·008	126-143
			Ethyl alcohol [14]	2·42-4·14	148-155
			Acetonitrile [129]	2·81-9·02	144-143
Diphenyl	$C_{12}H_{10}$	154	Acetonitrile [129]	1·96-7·44	171-159
Anthracene	$C_{14}H_{10}$	178	Anisol [70]	1·261-3·108	201·0-205·1
Nitromethane	CH_3NO_2	61	Nitrogen peroxide [134]	0·681-2·718	64·9-72
			Cyclohexane [125]	0·21-1·00	70·8-101·4
			Benzene [1]	0·29-2·32	57-63
Tetranitromethane	$C(NO_2)_4$	194	Dicyclohexane [124]	1·27-4·50	182·6-208·7
Nitroethane	$C_2H_5NO_2$	75	Cyclohexane [125]	0·37-3·37	91·1-135·7
			Nitrogen peroxide [134]	0·844-4·56	75·2-76·6
sec.-Nitropropane	$(CH_3)_2CHNO_2$	89	Benzene [1]	0·27-4·18	84-94
Nitrobenzene	$C_6H_5NO_2$	123	Ethylene bromide [62]	2·555-5·891	131-143
			Acetic acid [8, 52]	0·779-29·68	126-166
			Benzene [8]	0·902-32·32	119-149
m-Dinitrobenzene	$C_6H_4(NO_2)_2$	168	Ethyl alcohol [17]	5·912-12·57	181-211
p-Nitroanisol	$(NO_2)C_6H_4OCH_3$	153	Hexane [133]	2·733-4·661	170-175
Dimethoxynitrobenzene	$NO_2C_6H_3(OCH_3)_2$	183	Hexane [133]	1·100-3·567	202-246
Thiophene	C_4H_4S	84	Bromoform [4]	0·291-5·48	82·3-93·2
			Nitrobenzene [5]	0·519-19·55	85·2-100·8
			p-Bromotoluene [9]	0·498-22·60	78·6-105·4
Naphthalene picrate	$C_{10}H_8.C_6H_2(NO_2)_3OH$	357	Chloroform [27]	0·3096-3·346	164-195
			Benzene [27]	3·187-5·332	179-186
Bornylene nitrosite	$C_{10}H_{16}O_3N_2$	212	Acetone [114]	1·257-3·718	432-346

ELEMENTS.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Aluminium	Al_2	54	Iodine (cryos.) [77]	0·127-0·342	47·4-49·3
			Iodine (ebul.) [78]	0·179-0·793	50·5-62·6
Phosphorus	P_4	123	Methylene iodide [49]	0·23-0·60	122-124
		124	Carbon disulphide [79]	1·581-18·86	129-170
		123·8	Benzene [80, 87]	0·568-1·722	128·4-129·4
Arsenic	As	75·0	Sulphur (ebul.) [83]	0·435-1·583	117·5-131·1
Sulphur	S_8	256	Carbon disulphide [79, 80, 88, 90]	1·572-21·00	247-314
			Naphthalene [80, 90]	2·423-7·197	262·3-279·4

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
			Fenchone [81]	0·79-2·49	292-242
			Bromoform [82]	0·3094-1 048	254·5-257·9
			Aluminium bromide [84] (cryos.)	0·86-1·09	249-250
			Methylene iodide [49]	0·728-1·48	246-249
			Bromine [85]	0·34-1·05	52·5-62·8
			Chlorine [85]	0·73-0·93	217-274
			Disulphur dichloride [85]	0·92-8·58	43·6-89·0
			o-Nitrotoluene [86]	0·3186-0·3279	337-351
			Benzene [87]	0·2599-0·8501	189·9-195·4
			Phosphorus [89]	0·33-20·01	234·6-249·4
			Toluene [90]	?	288
			Diphenyl [90]	?	254
			Iodine [102]	0·38-2·36	225-263
Sulphur (rhombic)	S_8	256	Tin tetrachloride [85]	0·38-2·76	239-260
			Arsenic trichloride [85]	0·54-4·19	264-270
Sulphur (amorphous)	S_8	256	Tin tetrachloride [85]	0·67-2·57	238-251
Sulphur (monoclinic)	S_8	256	Arsenic trichloride [85]	0·78-3·76	233-256
Selenium	Se	79·2	Phosphorus [91]	0·203 0·480	624-614
			Sulphur [83] (ebul.)	0·905-4·066	191·6-191·3
			Methylene iodide [49]	0·302	796
			Disulphur dichloride [85]	0·94-2·93	64-69
Tellurium	Te	127·5	Sulphur [83] (ebul.)	1·19-3·55	169·4-169·1
			Iodine [102]	0·34-1·86	159-171·2
Iron	Fe_2	111·76	Iodine [78] (ebul.)	0·0847-0·311	112·5-110

ACIDS.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Hydrochloric acid	HCl	36·5	Nitrobenzene [44]	0·291-2·432	148·1-61·2
			Benzene [44]	0·036-1·744	101·8-62·9
			Acetic acid [2]	?	63·7
Nitric acid	HNO_3	63	Nitrobenzene [92, 135]	0·87-2·97	76·5-68·6
			Ethylene bromide [135, 92]	0·24-2·23	68·8-75·6
			Acetic acid [92, 135]	0·96-3·83	63-69·6
			Nitrogen peroxide [134]	0·687-3·52	82·6-89·6

			Monochloroacetic acid [135, 92]	0·93-5·40	66·3-71·5
			Phosphorus oxychloride [126]	1·08-3·19	58·8-59·7
Sulphuric acid	H_2SO_4	98	Acetic acid [135, 2]	1·74-8·42	252·6-190
			Nitrobenzene [135]	?	179·4-209·1
			Monochloroacetic acid [135]	1·95-7·66	182·0-142·7
			Benzene [92]	0·35-1·10	107·9-100·9
			Phosphorus oxychloride [126]	0·95-7·01	94·5-92·7
Phosphorous acid	H_3PO_3	82	Phosphorus oxychloride [126]	0·76	67·4
Boric acid	$B(OH)_3$	62	Formamide [42]	0·058-1·78	52·1-59·8
			Phenol [37]	2·35-14·74	65·7-65·0
Cacodylic acid	$(CH_3)_2$ ASOOH	138	Formamide [42]	0·403-19·15	137·9-143·8

OXIDES.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Water	H_2O	18	Bromoform [7]	0·0105-0·0196	18·9-23·5
			Ethylene bromide [7]	0·0144-0·0286	21·2-23·8
			Dimethylaniline [7]	0·0305-0·035	22·1-23·8
			p-Toluidine [29, 7]	0·452-1·602	28·69-33·29
			Methyl oxalate [7]	0·0825-1·820	20·6-35·9
			Methyl succinate [7]	0·236-2·13	21·3-32·5
			Veratrol [7]	0·0539-1·121	17·6-30·0
			Acetic acid [10]	0·214-17·82	18·5-32·4
			Phenol [29, 10]	0·903-1·329	19·38-19·62
Nitrogen trioxide	N_2O_3	76	Benzene [138]	0·441-1·337	83·2-83·0
Nitrogen peroxide	N_2O_4	92	Acetic acid [139]	0·92-8·97	94·6-90·3
Nitrogen pentoxide	N_2O_5	108	Phosphorus oxychloride [151]	0·496-1·169	105·7-108·2
Phosphorous oxide	P_4O_6	220	Benzene [150]	3·26	227
Boric anhydride	B_4O_6	140	Sulphuric acid [94]	0·96-2·69	142-152
Arsenious oxide	As_2O_3	198	Sulphuric acid [94]	0·92-1·97	288-455
			Antimony trichloride [85]	0·59-3·01	113-238
			Fenchone [81]	0·47-0·41	371-402
			Nitrobenzene [143]	1·0-2·1	399-448
Arsenic oxide	As_2O_5	230	Sulphuric acid [94]	0·526-2·59	192-179
Chlorine heptoxide	Cl_2O_7	182·9	Phosphorus oxychloride [151]	1·261-5·99	167-193
Molybdenum trioxide	MoO_3	144	Sulphuric acid [94]	0·852-4·32	275-290
Osmium tetroxide	OsO_4	255	Phosphorus oxychloride [151]	0·407-3·67	258-253

NON-METALLIC INORGANIC COMPOUNDS.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Phosphorus trichloride	PCl_3	136·33	Nitrobenzene [130]	0·93-1·35	124·6-125·8
Phosphorus oxychloride	$POCl_3$	153·35	Monochloroacetic acid [131]	0·29-5·47	125·8-179·9
Hydrogen phosphide (solid)	HP_2	63	Phosphorus [93]	0·0434-0·2179	360-375
Sulphur dichloride	SCl_2	103	Sulphur dioxide [39]	0·52-4·82	216-230
Disulphur dichloride	S_2Cl_2	134·9	Sulphur dioxide [39]	1·99-5·53	140-146
			Bromine [85]	0·52-2·31	131-125
Iodine monochloride	ICl	162·4	Phosphorus oxychloride [151]	2·06-5·88	168-164
			Acetic acid [152]	0·611-7.56	164-165
α-Iodine monochloride	ICl		Bromoform [151]	0·19-0·32	166-167
β-Iodine monochloride	ICl		Bromoform [151]	0·615-0·954	173-184
Iodine cyanide	ICN	153	Phosphorus oxychloride [151]	0·738-2·149	150-156

SALTS.

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Lithium chloride	LiCl	42·5	*n*-Propyl alcohol [94]	0·1824-5·01	36·19-48·95
			Bismuth chloride [95]	0·290-0·552	45·3-44·5
			Ethyl alcohol [97, 14, 38]	2·24-4·07	34·03-29·16
			iso-Amyl alcohol [96]	0·658-6·060	40·71·5
			Formic acid [41]	0·842-1·885	26·53-25 07
			Acetic acid [41, 98]	0·765-2·454	69·9-67·74
			iso-Butyl alcohol [97]	2·01-6·96	42·96-43·25
			iso-Amyl alcohol [97]	0·41-5·55	41·79-44·42
Lithium bromide	LiBr	86·86	Ethyl alcohol [97]	4·01 7·73	62·61-57·73
			iso-Butyl alcohol [97]	1·36-6·38	83·51-90·53
			iso-Amyl alcohol [97]	1·28-6·41	89·82 87·24
Lithium iodide	LiI	133·86	Ethyl alcohol [97]	5·70-11·02	100·7-98·81
			iso-Butyl alcohol [97]	0·84-6·55	129·8-141·7
			iso-Amyl alcohol [97]	1·77-11·96	154·4-157·5
			Acetic acid [97]	1·21-2·13	192·5 230·9
			Iodine [77] (cryos.)	0·267-10·45	416-678
Lithium nitrate	$LiNO_3$	68·95	Ethyl alcohol [97]	2·82 5·65	53·83 56·65
			iso-Butyl alcohol [97]	0·50-33·1	74·57-82·26
			iso-Amyl alcohol [97]	0·83-3·69	77·93-91·77
			Acetic acid [97]	0·46-1·55	78·05-102·3
Lithium acetate	CH_3COOLi	66·03	Acetic acid [99]	0·959-2·973	66-70

Lithium salicylate	C_6H_4 (OH) COOLi	144	*n*-Propyl alcohol [94]	1·973-15·45	246·8-288 9
Sodium chloride	NaCl	58·5	Bismuth chloride [95]	0·298-0·641	65 0-64·2
			Mercuric chloride [100]	0·51-2·00	57·2-58·5
Sodium bromide	NaBr	103	Formic acid [41]	0·341-4·644	36·85-38·50
			Formic acid [47]	1·522-4·995	76·22-72·1C
Sodium iodide	NaI	150	Acetic acid [41]	0·607-1·398	73·11-82·33
			Ethyl alcohol [14]	1·56-14·35	109-118
			Sulphur dioxide [69]	39·53	265
			n-Propyl alcohol [94]	3·09-14·02	140·1-150·5
			Iodine [77] (cryos.)	0·109-0·568	445-878
Sodium sulphate	Na_2SO_4	142	Acetic acid [97]	0·29-1·51	162·1-166·7
Sodium pyrosulphate	$Na_2S_2O_7$	222	Sulphuric acid [94]	0·71-2·68	122-106
Sodium acetate	CH_3COONa	82	Sulphuric acid [94]	1·27-2·39	234-250
			Acetic acid [14, 99]	1·11-6·91	69·0-77·1
Potassium chloride	KCl	74·6	Phenol [101]	0·1815-3·610	46·6-82·9
			Formic acid [41]	0·341-3·466	41·78-55·18
			Bismuth chloride [95]	0·487-12 06	70·8-73·4
			Mercuric chloride [100]	0·11-0·29	77·3 75·9
Potassium bromide	KBr	119·0	Formic acid [41]	2·201-6·542	80·9-77·3
Potassium iodide	KI	166	Sulphur dioxide [39, 69, 66]	1·85-14·58	235-317
			Iodine [77] (cryos.)	0·158-0·891	293-265
			Iodine [102, 78] (ebul.)	0·78-1·75	229·6-240·5
			Acetamide [140]	0·512-2·226	81·2-82·9
Potassium sulphate	K_2SO_4	174	Sulphuric acid [94]	1·74-3·17	136-130
Potassium hydrogen sulphate	$KHSO_4$	136	Sulphuric acid [94]	2·28-5·67	229-245
Potassium pyrosulphate	$K_2S_2O_7$	254	Sulphuric acid [94]	1·91-4·76	217-208
Potassium thiocyanate	KCNS	97	Sulphur dioxide [69, 66]	146·7-454·5 (N)	222-90
Potassium acetate	CH_3COOK	98·15	Acetic acid [99]	0·979-3·214	93-92
			Ethyl alcohol [14, 38]	1·16-10·87	82-102
Rubidium chloride	RbCl	120·9	Bismuth chloride [95]	0·830-1·267	113·7-115·6
			Mercuric chloride [100]	0·28-1·16	107-117
Rubidium iodide	RbI	212	Sulphur dioxide [69, 66]	72·46 (N)	376
			Iodine [77] (cryos.)	0·307 1·236	303-314
			Iodine [78] (ebul.)	0·367 1·80	244-307
Caesium chloride	CsCl	168·4	Bismuth chloride [95]	0·822-1·743	169·5-177·2
			Mercuric chloride [100]	0·34-1·13	153-158
Caesium iodide	CsI	259 9	Iodine [77] (cryos.)	0·400-1·618	380-373

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
			Iodine [78] (ebul.)	0·268-1·490	251-334
Ammonium chloride	NH_4Cl	53·4	Mercuric chloride [100]	0·07-0·34	45·9-53·8
			Formic acid [41]	0·362-2·888	38·45-41·12
Ammonium bromide	NH_4Br	97·9	Formic acid [41]	1·769-3·893	74·07-55·82
Ammonium iodide	NH_4I	145	Sulphur dioxide [69, 66]	93·46 (N)	345
Ammonium thiocyanate	NH_4CNS	76·2	Sulphur dioxide [66]	7·95 (N)	227
Cuprous chloride	CuCl	99·05	Bismuth chloride [95]	0·390-0·977	102·5-106·0
			Mercuric chloride [100]	0·32-0·77	125-155
			Quinoline [103]	0·289-10·93	107-174
		98·55	Pyridine [104]	0·41-0·82	118·7-122·1
			Methyl sulphide [104]	1·01-3·41	141-130
			Ethyl sulphide [104]	0·45 4·15	121-166
Cupric chloride	$CuCl_2$	134·5	Bismuth c loride [95]	0·583-0·983	125·8-127·2
		134	Pyridine [104]	1·58-4·02	136·06-139·41
			Methyl sulphide [104]	5·35-4·23	129-124
			Ethyl alcohol [98]	0·78-2·508	130·0-147·1
			Acetone [98]	0·259-7·94	173·1-194·9
			Urethane [138, 140]	0·48-0·77	271·1-263·7
			Acetamide [140]	0·801-2·127	76·5-81·3
Cuprous bromide	CuBr	142·99	Pyridine [104]	0·49-3·14	148·90-145·39
		143·5	Methyl sulphide [104]	1·60-5·18	147-132
		142·9	Ethyl sulphide [104]	1·56 5·39	221-219
Cuprous cyanide	CuCN	89·16	Pyridine [104]	0·14-1·08	175·30-184·5
Silver chloride	AgCl	286·06	Piperidine [104]	0·82-2·47	326·29-360·08
		143·4	Bismuth chloride [95]	1·046-2·189	140·8-145·99
Silver bromide	AgBr	374·84	Piperidine [104]	0·94-4·13	438·15-442·56
Silver iodide	AgI	468·40	Piperidine [104]	0·82-2·18	462·81-480·83
Silver nitrate	$AgNO_3$	170	Urethane [136]	0·37	173·6
		169·61	Piperidine [104]	0·97-6·09	188·32-383·83
		169·97	Pyridine [105, 104, 72]	1 65-17·68	161-215
			Benzonitrile [129, 104]	1·49-3·51	220-239
			Acetonitrile [129]	1·69-9·42	135-144
Silver cyanide	AgCN	134	Pyridine [72]	0·586-1·911	237-228
Silver thiocyanate	AgCNS	166	Pyridine [72]	0·290-1·749	207-184
Glucinum chloride	$GlCl_2$	79·77	Pyridine [106]	0·383-0·763	78·46-84·50

Magnesium formate	$(HCOO)_2Mg$	114	Formic acid [2]	?	229·6
Magnesium acetate	$(CH_3COO)_2Mg$	142	Acetic acid [2]	?	304·3
Calcium chloride	$CaCl_2$	111	Bismuth chloride [95]	0·227-0·356	113·8-115·1
Calcium iodide	CaI_2	293·8	Iodine [102]	1·81-4·67	1043-1165
Calcium acetate	$(CH_3COO)_2Ca$	158	Acetic acid [99]	0·839-1·824	214-226
Strontium chloride	$SrCl_2$	158·6	Bismuth chloride [95]	0·212-0·460	163·9-165·4
Strontium iodide	SrI_2	341·3	Iodine [102]	1·65-4·95	900·6-1077
Strontium acetate	$(CH_3COO)_2Sr$	205·6	Acetic acid [99]	0·839 1·824	214-226
Barium chloride	$BaCl_2$	208·3	Bismuth chloride [95]	0·771-1·719	210·0-214·6
Barium acetate	$(CH_3COO)_2Ba$	255·4	Acetic acid [99]	1·500-4·839	253-254
Zinc chloride	$ZnCl_2$	136·3	Bismuth chloride [95]	0·608 1·037	137·9-141·5
			Quinoline [103]	0·195-6·772	146-137
		136	Piperidine [104]	1·45-2·65	147·69-168·36
			Urethane [136]	0·70	138·7
			Pyridine [104]	0·96-3·10	125·07-129·23
			Methyl sulphide [104]	0·93-4·18	245-211
Zinc bromide	$ZnBr_2$	225·3	Quinoline [103]	0·721-3·535	223-226
		224·4	Pyridine [104]	0·87-3·15	212·96-208·54
		225	Methyl sulphide [104]	0·93-4·18	245-211
			Aluminium bromide [84]	2·93-8·12	215 220
Zinc iodide	ZnI_2	319·1	Quinoline [103]	0·498-2·381	306-325
			Methyl sulphide [104]	1·61-7·59	310-316
Cadmium chloride	$CdCl_2$	183·3	Bismuth chloride [95]	0·887-1·491	187·3-193·1
			Quinoline [103]	1·300-7·498	183-187
			Urethane [136]	0·44	183·1
Cadmium bromide	$CdBr_2$	272·3	Quinoline [103]	2·618-10·85	269-275
		271·22	Piperidine [104]	2·10-9·97	280·2-329·4
		272	Aluminium bromide [84]	0·22	259
Cadmium iodide	CdI_2	366·3	Quinoline [103]	2·287-11·57	377-364
		366	Ethyl alcohol [14, 38, 108]	2·59-27·84	324-313
			Water [14, 38, 107, 108]	4·36-21·20	366-364
			Piperidine [104]	1·78-14·59	343·1-397·7
			Pyridine [104]	0·80-3·56	395·9-329·2
			Methyl sulphide [104]	1·32-8·48	346-372
			Ethyl sulphide [104]	1·73-8·52	356-375
Mercuric chloride	$HgCl_2$	271	Ethyl alcohol [14, 53, 38]	2·93-30·08	265-271

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
			Water [53, 38]	{8·978-4·253 {19·70-13·54	260·8-263·3 329-335
			Methyl sulphide [104]	0·84-3·69	238-275
			Ethyl sulphide [104]	2·56-10·46	272-280
			Benzonitrile [129, 104]	1·72-4·02	300-335
			Fenchone [81]	1·12-9·07	275-282
			Urethane [136]	0·66-3·78	268·5-272·3
Mercurous chloride	Hg_2Cl_2	471	Mercuric chloride [100]	0·59-2·16	471-459
Mercuric bromide	$HgBr_2$	360	Fenchone [90]	1·02-6·47	355-369
			Aluminium bromide [84]	0·18-5·95	346-500
Mercuric iodide	HgI_2	454	Ethyl alcohol [109]	1·877	428
			Pyridine [104]	0·91-3·32	283·8-318·9
			Methyl sulphide [104]	1·89-12·23	463-460
			Ethyl sulphide [104]	1·53-5·66	464 452
			Benzonitrile [104, 129]	0·731-2·20	435-513
			Fenchone [81]	0·92-4·95	403-458
Mercury methyl chloride	$HgCH_3Cl$	251	Methyl sulphide [104]	1·64-6·86	263-246
			Ethyl sulphide [104]	1·87-7·14	254-259
Mercury methyl iodide	$HgCH_3I$	342	Methyl sulphide [104]	3·01-7·78	353-320
			Ethyl sulphide [104]	2·97-11·15	348-338
Mercuric cyanide	$Hg(CN)_2$	252	Pyridine [104]	0·79-3·31	229·8-210·8
Thallous chloride	TlCl	239·5	Mercuric chloride [100]	0·37-1·37	218-233
Aluminium chloride	$AlCl_3$	133·5	Ether [49]	3·14-13·79	137-189
			Pyridine [104]	0·72-2·38	125·9-128·4
			Nitrobenzene [110]	0·96-4·52	130-131
			Aluminium bromide [84]	0·50-5·07	125-133
Aluminium bromide	$AlBr_3$	267	Bromine [49, 85]	3·453-11·50	528-584
			Carbon disulphide [110]	1·5-10·9	539-540
			Nitrobenzene [110]	8·22-15·91	275-277
Aluminium iodide	AlI_3	408	Aluminium bromide [84]	1·43-6·66	400-409
			Carbon disulphide [110]	2·5-10·7	824-826
Stannous chloride	$SnCl_2$	189	Pyridine [104]	0·40-3·36	210·6-191·0
			Ethyl sulphide [104]	1·65-4·56	175-176
			Urethane [136]	1·36-4·90	183·8-182·9

Stannic chloride	$SnCl_4$	258·87	Nitrobenzene [130]	2·13-6·83	445·9-290·4
Stannous bromide	$SnBr_2$	278·32	Pyridine [104]	0·66-4·13	264·1-276·2
		278	Ethyl sulphide [104]	1·56-4·28	283-236
Stannic bromide	$SnBr_4$	439	Bromine [49]	1·88-10·35	434-441
Lead chloride	$PbCl_2$	277·8	Bismuth chloride [95]	1·064-1·797	275·2-285·8
Lead nitrate	$Pb(NO_3)_2$	330·35	Pyridine [104]	1·27-4·43	345·50-363·28
Lead acetate	$(CH_3COO)_2$ Pb	324·9	Acetic acid [99]	2·177-4·878	324 328
Arsenic trichloride	$AsCl_3$	181·4	Carbonyl chloride [39]	3·39-11·10	189-194
			Nitrobenzene [130]	0·40-10·45	126·7-175·7
Arsenious bromide	$AsBr_3$	315	Bromine [49]	1·91-5·94	312-320
Arsenious iodide	AsI_3	455·7	Carbon disulphide [111]	5·65-9·89	442-466
			Fenchone [81]	1·00-3·20	442-457
Arsenious sulphide	As_2S_3	246·0	Sulphur [83]	0·67-2·65	117·5-131·1
Antimony trichloride	$SbCl_3$	226·6	Carbonyl chloride [39]	0·60-3·04	242-255
			Chloroform [111]	6·39-11·10	262-284
			Nitrobenzene [130]	2·58-10·65	255·6-211·9
Antimony pentachloride	$SbCl_5$	297·3	Carbonyl chloride [39]	0·60-3·41	314-332
Antimony tribromide	$SbBr_3$	360	Chloroform [111]	5·11-9·90	383-420
			Aluminium bromide [84]	1·62-12·96	377-825
Antimony pentabromide	$SbBr_5$	520	Bromine [49]	3·40-7·96	532-550
Antimony triiodide	SbI_3	501	Carbon disulphide [111]	2·46-3·54	462-502
			Fenchone [81]	1·81-4·40	500-498
Antimony sulphide	Sb_2S_3	336·0	Sulphur [83]	0·504-7·095	198·1-185·4
Bismuth chloride	$BiCl_3$	312·08	Nitrobenzene [130]	0·68-3·08	203·9-326·9
Bismuth bromide	$BiBr_3$	448	Aluminium bromide [84]	0·89-10·57	450-1677
Bismuth iodide	BiI_3	589	Fenchone [81]	0·60-1·29	503-599
Bismuth acetate	$(CH_3COO)_3$ Bi	385·5	Acetic acid [99]	1·852-6·163	369-382
Manganous chloride	$MnCl_2$	126	Urethane [136, 140]	0·72-3·09	131·3-141·2
			Acetamide [140]	1·124-3·453	51-54·7
Ferric chloride	$FeCl_3$	162·3	Ether [49]	1·53-5·43	170-185
			Ethyl alcohol [49]	2·37-11·57	195-163
			Pyridine [105, 104]	2·63-13·75	130-150
			Nitrobenzene [130]	1·479-4·739	316·9-190·8
Ferrous chloride	$FeCl_2$	126·6	Pyridine [104]	0·33-0·78	112·3-107·9
Cobalt chloride	$CoCl_2$	130	Urethane [136, 140]	0·48-0·90	256·4-253·8
			Bismuth chloride [95]	0·451-0·688	127·6-124·9
			Quinoline [103]	0·396-2·945	132-146

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
			Piperidine [104]	0·50	145·17
			Pyridine [104]	0·41-1·96	128·99-123·33
			Acetamide [140]	0·481-1·772	62·4-74·8
Cobalt bromide	$CoBr_2$	218·9	Pyridine [104]	0·20-2·99	202·72-216·56
			Quinoline [103]	1·197-7·224	223-230
Nickel chloride	$NiCl_2$	129·6	Quinoline [103]	0·669-4·590	130-135
Nickel bromide	$NiBr_2$	218·6	Quinoline [103]	0·790-4·495	225-235
Methylammonium chloride	CH_3NH_3Cl	67·5	Sulphur dioxide [66]	69·5 (N)	119
Dimethylammonium chloride	$(CH_3)_2\ NH_2Cl$	81·6	Sulphur dioxide [66]	14·4-73·6 (N)	109-99·8
			Chloroform [111, 116, 115]	0·47-3·18	227-333
			Phenol [101]	0·335-9·309	69·1-83·1
Trimethylammonium chloride	$(CH_3)_3\ NHCl$	95·6	Sulphur dioxide [66]	4·77-75·0 (N)	96·5-87·9
Tetramethylammonium chloride	$(CH_3)_4\ NCl$	109·6	Sulphur dioxide [66]	10·6-75·7 (N)	1·08-96·1
Tetramethylammonium bromide	$(CH_3)_4NBr$	154·1	Sulphur dioxide [66]	15·6-61·1 (N)	160-135
Tetramethylammonium iodide	$(CH_3)_4\ NI$	201·0	Sulphur dioxide [66, 69]	14·6-56·6 (N)	167-162
			Phenol [101]	0·205-6·232	135·5-189·0
			Iodine [102]	0·46-1·19	257·4-273
Ethylammonium chloride	$C_2H_5NH_3Cl$	81·57	Sulphur dioxide [66]	23·7-107·9 (N)	123-197
Diethylammonium chloride	$(C_2H_5)_2\ NH_2Cl$	109·6	Chloroform [111, 115]	1·87-6·29	275-369
			Bromoform [117]	0·233-3·575	300-463
			Formamide [42]	0·207-0·774	56·6-57·9
			Water [118]	73·51-26·40 (*n*)	68·08-63·54
			Ethyl alcohol [118]	164·4-51·16 (*n*)	117·6-111·6
			Diphenylamine [118]	6·66-36·50 (*n*)	194·2-226·6
			Phenol [118]	7·65-43·57 (*n*)	137·7-136·6
			Acetic acid [118]	7·86-121·00 (*n*)	129·9-220·3
			iso-Amyl alcohol [118]	63·47-25·76 (*n*)	193·7-152·9
			Formic acid [118]	12·46-55·03 (*n*)	79·45-78·12
Diethylammonium nitrate	$(C_2H_5)_2\ NH_2NO_3$	136	Formamide [42]	0·617-1·062	68·6-69·1
Triethylammonium chloride	$(C_2H_5)_3\ NHCl$	137·6	Chloroform [111, 115]	3·58-7·11	213-253
			Bromoform [117]	0·328-3·591	194-381
			Water [118]	(cryos.) 5·84-36·86 (*n*)	68·64-79·16
				(ebul.) 40·36-17·03(*n*)	81·75-71·36
			Ethyl alcohol [118]	94·43-37·35 (*n*)	124·0-126·5

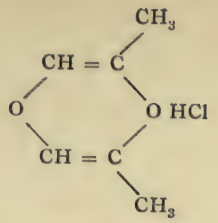
Triethylammonium bromide	$(C_2H_5)_3$ NHBr	182	Diphenylamine [118]	6·03-56·66 (*n*)	143·0-202·8
			Phenol [118]	8·92-42·80 (*n*)	148·4-153·5
			Acetic acid [118]	4·37-51·25 (*n*)	156·5-229·9
			iso-Amyl alcohol [118]	38·56-15·41 (*n*)	164·7-155·8
			Formic acid [118]	4·55-36·74 (*n*)	93·76-93·80
Triethylammonium iodide	$(C_2H_5)_3$ NHI	229	Chloroform [111]	3·74-9·34	294-403
			Bromoform [117]	0·659-3·166	328-681
			Water [118]	62·95-18·75 (*n*)	118·4-112·9
			Ethyl alcohol [118]	121·9-34·38 (*n*)	192·2-171·1
			Diphenylamine [118]	7·19-35·06 (*n*)	203·9-309·6
			Phenol [118]	6·64-13·43 (*n*)	217·3-225·0
			Acetic acid [118]	3·21-32·82 (*n*)	227·4-350·4
			iso-Amyl alcohol [118]	56·43-19·42 (*n*)	245·5-199·8
Tetraethylammonium chloride	$(C_2H_5)_4$ NCl	165·6	Chloroform [111]	4·51-7·90	498-686
			Bromoform [117]	0·353	428
			Water [118]	52·69-18·69 (*n*)	144-103·1
			Ethyl alcohol [118]	81·39-23·74 (*n*)	272·6-250·2
			Diphenylamine	3·11-33·17 (*n*)	212·6-446·7
			Phenol	8·93-29·00 (*n*)	279·5-301·3
			Acetic acid	5·86-13·16 (*n*)	446·6-458·2
			iso-Amyl alcohol	44·70-14·46 (*n*)	384·8-273·0
			Formic acid	7·38 (*n*)	180·8
Tetraethylammonium bromide	$(C_2H_5)_4$ NBr	210·1	Chloroform [111]	2·00-6·43	646-976
			Water [118]	47·97-18·92 (*n*)	101·3-93·40
			Ethyl alcohol [118]	54·54-21·76 (*n*)	146·3-150·8
			Phenol [118]	5·73-12·60 (*n*)	194·8-206·0
			iso-Amyl alcohol [118]	22·13-70·73 (*n*)	173·6-218·6
Tetraethylammonium iodide	$(C_2H_5)_4$ NI	257·1	Chloroform [111]	4·26-7·97	1410-1794
			Water [118]	56·37-12·69 (*n*)	134·0-117·4
			Ethyl alcohol [118]	39·81-10·66 (*n*)	186·7-177·1
			Acetic acid [118]	5·36-42·26 (*n*)	255·1-580·3
			iso-Amyl alcohol [118]	34·49-13·78 (*n*)	326·3-312·7
			Sulphur dioxide [66, 69]	6·41-42·9 (*n*)	236-190
			Methyl alcohol [119]	4·383-8·867	199·0-208·1
			Ethyl alcohol [119]	1·533-3·609	202·7-230·3
			Acetonitrile [119]	2·233-5·492	163·1-175·0
			Propionitrile [119]	1·402-3·091	167·0-182·9

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
			Nitromethane [119]	1·805-4·778	147·3-166·3
			Ethylene cyanide [144]	0·593-1·232	134·3-142·4
			Pyridine [105]	0·71-1·45	315-351
			Formamide [42]	0·170-3·459	132·3-142·5
			Water [118]	32·15-19·75 (*n*)	171·2-164·8
			Ethyl alcohol [118]	49·75-21·76 (*n*)	319·3-251·8
			Phenol [118]	7·24-30·52 (*n*)	296·9-317·1
			iso-Amyl alcohol [118]	24·28-7·73 (*n*)	469·8-358·9
			Formic acid [118]	12·81-37·41 (*n*)	171·8-186·1
			Diphenylamine [118]	22·44-45·6 (*n*)	1414-949
n-Propylammonium chloride	$C_3H_7NH_3Cl$	95·5	*p*-Toluidine	5·75-28·74 (*n*)	410·1-358·0
Dipropylammonium chloride	$(C_3H_7)_2\ NH_2Cl$	137·5	Chloroform [111]	0·88-1·58	443-588
			Chloroform [111]	2·72-6·75	282-320
			Bromoform [117]	0·674-3·332	354-382
Tetrapropylammonium chloride	$(C_3H_7)_4\ NCl$	221·7	Chloroform [111, 115]	3·78-10·43	716-517
Tetrapropylammonium bromide	$(C_3H_7)_4\ NBr$	266·1	Chloroform [111]	4·70-10·95	1011-965
Tetrapropylammonium iodide	$(C_3H_7)_4\ NI$	313·1	Chloroform [111, 115]	3·21-13·42	1254-1393
			Water [118]	32·60-11·61 (*n*)	223·5-152·9
			Ethyl alcohol [118]	47·90-14·85 (*n*)	325·9-290·0
			Diphenylamine [118]	8·99-24·44 (*n*)	1285-1377
			Phenol [118]	6·59 16·79 (*n*)	380·5-421·7
			Acetic acid [118]	5·25-31·65 (*n*)	578·9-1263·5
			iso-Amyl alcohol [118]	30·42-13·36 (*n*)	679·0-627·2
			Acetone [118]	13·74-7·97 (*n*)	329·4-284·0
			Formic acid [118]	3·63-29·86 (*n*)	182·1-230·6
Tetrapropylammonium nitrate	$(C_3H_7)_4\ NNO_3$	248·2	Chloroform [111]	4·24-9·52	1243-1289
		248·4	Water [118]	25·54-16·83 (*n*)	182·6-150·8
			Ethyl alcohol [118]	67·79-21·39 (*n*)	230·8-219·4
			Diphenylamine [118]	4·34-25·83 (*n*)	619·7-978·1
			Phenol [118]	5·05-28·33 (*n*)	288·4-312·4
			Acetic acid [18]	2·41-23·66 (*n*)	307·6-519·0
			iso-Amyl alcohol [118]	36·38-9·22 (*n*)	417·3-348·0
			Acetone [118]	57·09-24·01 (*n*)	342·3-282·9
iso-Butylammonium chloride	$(C_4H_9)\ NH_3Cl$	109·6	Chloroform [111]	2·81-5·88	522-533

iso-Butylammonium iodide	$(C_4H_9)_4$ NI	201·1
iso-Amylammonium chloride	(C_5H_{11}) NH_3Cl	123·6
Di-*iso*-amylammonium chloride	$(C_5H_{11})_2$ NH_2Cl	193·6
Tetra-*iso*-amylammonium iodide	$(C_5H_{11})_4$ NI	427·3
Aniline hydrochloride	$C_6H_5NH_2.HCl$	129·6
Methylaniline hydrochloride	$C_6H_5NH(CH_3).HCl$	143·5
Ethylaniline hydrochloride	$C_6H_5NH(C_2H_5).HCl$	157·6
Ethylaniline hydriodide	$C_6H_5NH(C_2H_5).HI$	249·1
Diethylaniline hydrochloride	$C_6H_5N(C_2H_5)_2.HCl$	158·6
Diethylaniline hydriodide	$C_6H_5N(C_2H_5)_2.HI$	277·0
Benzylammonium chloride	$C_6H_5CH_2NH_3Cl$	143·6
Dibenzylammonium chloride	$(C_6H_5CH_2)_2$ NH_2Cl	233·5
Tribenzylammonium chloride	$(C_6H_5CH_2)_3$ NHCl	323·6
Methylpropylphenylbenzylammonium bromide	$CH_3.C_3H_7.C_6H_5.(C_6H_5CH_2)NBr$	320
Methylpropylphenylbenzylammonium iodide	$CH_3.C_3H_7.C_6H_5.(C_6H_5CH_2)NI$	366·8
Methylallylphenylbenzylammonium bromide	$CH_3.C_3H_5.C_6H_5.(C_6H_5CH_2)NBr$	318
Methyl*iso*-butylphenylbenzyl ammonium iodide	$CH_3.C_4H_9.C_6H_5.(C_6H_5CH_2)NI$	380·8

Bromoform [117]	0·314-1·452	435-466
Ethyl alcohol [118]	163·6-29·18 (*n*)	116·4-110·6
Phenol [118]	16·80-53·27 (*n*)	136·0-145·3
Acetic acid [118]	9·59-64·22 (*n*)	155·0-204·2
iso-Amyl alcohol [118]	62·63-19·34 (*n*)	185·8-173·8
Water [118]	119·0-51·39 (*n*)	67·61-61·06
Chloroform [111]	4·67-9·58	990-1443
Chloroform [111, 115]	2·77-5·37	739-703
Formamide [42]	0·200-0·634	65·6-69·6
Formamide [42]	0·229-0·307	99·0-100·4
Chloroform [111]	3·15-5·17	528-636
Bromoform [117]	0·431-4·015	667-1463
Phenol [101]	0·2497-11·510	128·3-170·8
Chloroform [111]	2·33-5·50	308-351
Bromoform [117]	1·176-4·448	366-369
Chloroform [111]	2·40-4·49	346-353
Water [118]	42·36-19·32	100·0-85·1
Ethyl alcohol [118]	96·56-30·31 (*n*)	192·8-169·2
iso-Amyl alcohol [118]	50·00-14·07 (*n*)	270·3-320·7
Acetic acid [118]	4·78-41·21 (*n*)	217·4-271·9
Chloroform [111]	3·73-7·51	504-569
Chloroform [111]	3·35-7·88	256-294
Bromoform [117]	0·394-3·895	237-443
Chloroform [111]	5·62-10·25	528-616
Bromoform [117]	0·693-3·132	487-934
Sulphur dioxide [66]	7·87-84·9 (N)	182-309
Chloroform [111]	0·48-0·79	487-481
Chloroform [111]	2·98-4·68	392-397
Bromoform [117]	0·508-1·663	362-404
Bromoform [120]	0·724	704·8
Bromoform [120]	0·286	786
Bromoform [120]	1·692	765·1
Bromoform [120]	0·295	754

Substance.	Formula.	M.W. (Calcd.).	Solvent.	Concentration.	M.W. (Obs.).
Methylallylphenylbenzylammonium *d*-camphor sulphonate	$CH_3.C_3H_5.C_6H_5.(C_6H_5CH_2)NO_3SC_{10}H_{15}O$	471	Bromoform [120]	0·804	964
Quinoline hydrochloride	$C_9H_7N.HCl$	165·5	Chloroform [111]	3·62-12·37	328-437
Quinoline hydrobromide	$C_9H_7N.HBr$	210·0	Chloroform [111]	4·27-10·92	480-664
Quinoline hydriodide	$C_9H_7N.HI$	257·0	Chloroform [111]	0·78-1·35	297-414
Quinoline ethiodide	$C_9H_7NC_2H_5I$	285·0	Chloroform [111]	0·60-1·34	456-687
			Water [118]	51·60-19·7 (*n*)	225·8-153·3
			Ethyl alcohol [118]	39·15-13·49 (*n*)	360·4-291·2
			iso-Amyl alcohol [118]	22·30-8·38 (*n*)	600·3-392·2
Ethylphenylhydrazine hydrochloride	$C_6H_5NH.NHC_2H_5.HCl$	172·6	Chloroform [111]	3·50-8·32	430-535
Pyridine methiodide	$C_5H_5N(CH_3)I$	221	Diphenylamine [121]	1·421-2·435	833-892
			Water [121]	1·323-2·194	111-119
Quinoline methiodide	$C_9H_7NCH_3I$	271	Chloroform [121]	8·973	227
			Diphenylamine [121]	0·625-2·489	423-644
			Water [121]	1·375-4·145	134-166
Phenylacridine methiodide	$C_6H_5.C(C_6H_4)_2\ N.CH_3I$	397	Diphenylamine [121]	0·647-2·024	436-685
Phenylacridonium chloride	$C_6H_5C.(C_6H_4)_2\ NHCl$	292	Chloroform [115]	0·45-1·09	374-384
Phenylacridonium iodide	$C_6H_5C.(C_6H_4)_2\ NHI$	383	Chloroform [115]	1·265-2·371	555-502
Methylphenylacridonium chloride	$C_6H_5C(C_6H_4)_2NCH_3Cl$	305·5	Chloroform [115, 121]	0·830-3·512	599-817
			Alcohol [122]	3·32	263
Methylphenylacridonium bromide	$C_6H_5C.(C_6H_4)_2\ NCH_3Br$	350	Chloroform [115, 122]	2·512	790
				1·523	424
			Alcohol [122]	5·193	341
Methylphenylacridonium iodide	$C_6H_5C.(C_6H_4)_2\ NCH_3I$	397	Chloroform [115, 122, 121]	1·920-6·963	1952-2240
			Alcohol [122]	5·669	362
Methylphenylacridonium thiocyanate	$C_6H_5C.(C_6H_4)_2\ N.SCN$	328	Chloroform [115]	1·020-3·351	1075-1405

Dimethylpyrone hydrochloride		160·5	Bromoform [117]	0·269-1·181	305-421
Trimethylsulphonium iodide	$(CH_3)_3SI$	204	Chloroform [111]	4·83	310
Triethylsulphonium chloride	$(C_2H_5)_3$ SCl	154·6	Sulphur dioxide [66, 69]	6·12-55·5 (N)	181-260
Triethylsulphonium bromide	$(C_2H_5)_3$ SBr	199·1	Chloroform [111]	2·72-5·68	599-714
Triethylsulphonium iodide	$(C_2H_5)_3$ SI	246·1	Chloroform [111]	4·02-8·50	949-1359
			Chloroform [111]	5·73-12·48	1765-2951

The following substances or groups of substances have the normal molecular weight in a variety of solvents: sucrose and mannitol [14, 38, 53]; halogen derivatives of pseudocuminol and p-xylenol [20]; acylcresols [24]; halogen derivatives of benzene azophenol [20]; pseudocuminolazophenol [20]; benzene- and tolueneazo-cresols, xylenols, pseudocuminols and naphthols [20]; alkyloxy derivatives of benzene azophenol [20]; thiophenol, its halogen and alkyloxy derivatives [11, 1]; ethers and esters [1, 8, 12, 14, 19] (except when containing an associating group); camphor [7, 8, 12, 14, 18]; benzil [14, 37, 51, 54]; quinones [1, 51]; secondary and tertiary amines [11, 12, 54, 71, 146]; hydrazones [20]; azoles and thienyls [12, 51]; azobenzene, its amido and oxyderivatives [1, 38]; hydrocarbons (see note at head of Appendix) [15, 27, 33, 35, 38, 51, 54, 66, 69, 75, 145, 146]; halogen derivatives of hydrocarbons [111, 84]; nitro-derivatives of aromatic hydrocarbons (see also note above) [33]; nitroso-benzene and toluene and their halogen derivatives [24, 132]; iodine [8, 145, 147]; organic solutes dissolved in salt hydrates [148].

Addendum.

Published too late for inclusion in the above tables may be mentioned the determinations of the degree of association in nitrobenzene of phenols, alcohols, aromatic and aliphatic acids, aldehydes, ketones, acid anhydrides, amines, amides, anilides, methane and benzyl nitrile by Böeseken and van der Eerden [153].

Note on Molecular Weights of Pure Liquids.

The molecular weights of substances in the liquid condition so far determined are of doubtful value. An excellent summary of measurements depending on surface tension measurements is given in the publication by Walden and Swinne (loc. cit., p. 115). In addition may be mentioned an investigation by Walden of the molecular magnitudes of molten organic ammonium salts. (Bull. Acad. Sci. St. Pétersbourg, 1914, p. 405.)

December, 1914.

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